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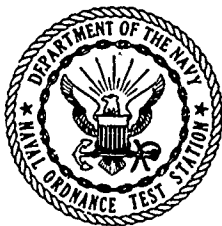
CARBOXYL-TERMINATED POLYHYDROCARBONS

SUMMARY REPORT FOR THE PERIOD OF
1 July 1964—30 June 1966

by

Minnesota Mining and Manufacturing Company
for the
Propulsion Development Department

ABSTRACT. Procedures were developed for the preparation of one pound lots of carboxyl-terminated polybutadiene (CTPB) by free radical polymerization using two different initiators. Several samples of varying molecular weights were prepared for further evaluation as propellant binders. Several initiator systems for the preparation of CTPB by anionic methods were investigated. The effects of a number of polymerization parameters were determined using a dilithiopolyisoprene initiator. Problems were encountered in the determination of solution viscosities and molecular weights of CTPB. Evidence was obtained for association of CTPB in solution and gel permeation chromatography produced some anomalous results.



U. S. NAVAL ORDNANCE TEST STATION
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FOREWORD

This report summarizes the work carried out by the Minnesota Mining and Manufacturing Company in its Central Research Laboratories during the period 1 July 1964 through 30 June 1966 under Contract Number N123 (60530)50116A. It was edited by J. H. Prager and E. E. Rice.

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SUMMARY

Procedures were developed for the preparation of one pound lots of carboxyl-terminated polybutadiene (CTPB) by free radical polymerization. Two initiators, glutaric acid peroxide (GAP) and 4,4'-azo-bis (4-cyanopentanoic acid) (ABCPA) were used. Best results were obtained when a solution of the initiator was fed continuously to a solution of butadiene in the polymerization solvent. Conversions were of the order of 30-40%. The polymerization was found to be reproducible and molecular weight of the polymer could be accurately controlled by varying the concentration of the initiator. Several different procedures were employed for purification of the polymers depending upon the molecular weight and the initiator used. A number of one-pound samples of radical-initiated CTPB were shipped to NOTS for further evaluation.

Several initiator systems for the preparation of CTPB by anionic methods were investigated. Preliminary experiments indicated that a hydrocarbon soluble initiator was most suitable. The polymerization of butadiene using low molecular weight dilithiopolyisoprene (prepared from lithium 2-methylnaphthalene and isoprene) as the initiator was studied in some detail. Freshly prepared initiator, free from other initiating species such as metallic lithium and lithium 2-methylnaphthalene, was found to be essential for preparation of satisfactory polymer. Evidence was obtained indicating that the carbonation step of the reaction generally gave some chain-extension of the polymer, resulting in an undesirable broad molecular weight distribution.

Several problems were noted in the characterization of CTPB. While values of acid equivalent weights appeared to be accurate and reproducible, molecular weight measurements by VPO were found to be erratic and unreliable. The difficulty encountered in the molecular weight measurements is probably due to a combination of sample inhomogeneity, the presence of substantial amounts of low molecular weight impurities in CTPB samples and "association" effects of CTPB in solution, in addition to a considerable error in the method in the molecular weight range of interest.

Evidence for association of CTPB in solution was also obtained by viscosity measurements, and gel permeation chromatography of CTPB gave some anomalous results.

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I. INTRODUCTION

Carboxyl-terminated polybutadiene (CTPB) prepolymers appear to have considerable promise for use as a composite binder. However, problems have been noted in reproducibility of physical properties of propellants using CTPB of different manufacturers and different lots. A lack of adequate specifications based on meaningful properties is believed to be the cause of these problems.

The objective of this project is to gain a thorough understanding of the procedures used to prepare and characterize CTPB and through this knowledge, relate variations in properties of the prepolymer to final propellant properties. It is hoped that this approach will produce data from which adequate specifications for prepolymer manufacture can be formulated.

II. DISCUSSION

A. RADICAL POLYMERIZATION

General Considerations. — One of the methods of preparation of carboxyl-terminated polybutadiene (CTPB) involves the use of a dicarboxyl - containing radical initiator. Polymer produced in such a system will have exclusively carboxyl ends only if termination occurs completely by coupling. To the extent that disproportionation takes place, non-carboxyl ends will be formed. Chain transfer will also, of course, generally produce non-functional ends.

Branching introduces an added complication into the preparation of radical-initiated CTPB, since multichain polymers are thereby formed. It is, of course, very difficult to determine whether there are non-functional ends present in a mixture of branched and unbranched species as shown in Figure 1.

Polymerization Procedure. Butadiene is slow to polymerize by a radical mechanism. Table I shows its low propagation rate constant in comparison to that of several other monomers.

Table I. Absolute Rate Constants for Propagation¹

Monomer	k_p at 60° C. (l./mole sec.)
Vinyl acetate	3700
Methyl acrylate	2090
Methyl methacrylate	367
Styrene	176
Butadiene	100
Isoprene	50

When high molecular weight polybutadiene is sought, it is necessary to polymerize in emulsion in order to produce polymer at a reasonable rate. Since a low molecular weight product is desired in the case of carboxyl-terminated butadiene pre-polymer, solution polymerization can be employed with a very large charge of initiator.

However, it is necessary to operate at a relatively high reaction temperature in order to achieve a suitable rate of polymerization.

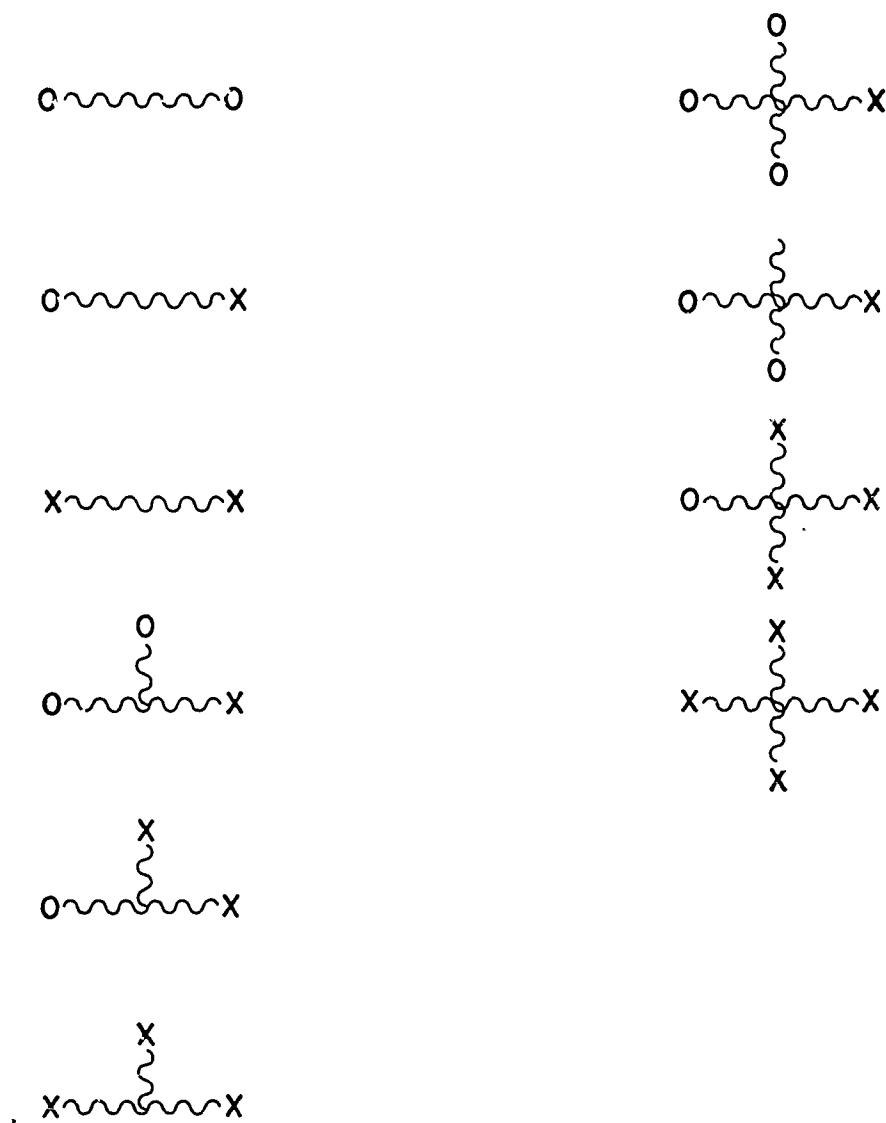


FIGURE 1. Linear and Branched Chains with Functional and Non-Functional Ends.

Table II shows two glutaric acid peroxide-initiated runs carried out at 70° and 90° C., respectively. At 70° C., the conversion was only 14% in four hours; at 90° C. it had increased to 25%.

Table II. Effect of Polymerization Temperature on Conversion with Single Charge of Glutaric Acid Peroxide (GAP) Initiator.

Run No.	Butadiene (g.)	GAP (g.)	Tetrahydrofuran (cc.)	Temp. (°C.)	Time (hr.)	Conv. (%)	$\langle \eta \rangle$ (1% in C_6H_6).
24B1	5	0.6	15	70	4	14	.11
24B2	5	0.6	15	90	4	25	.12

As the temperature of polymerization is increased, however, the rate of generation of initiator radicals also increases. Table III shows three runs, initiated with 4,4'-azo-bis (4-cyanopentanoic acid). The conversions were identical within experimental error for runs of two, five, and twenty hours, indicating that no significant amount of initiator remains after two hours at this temperature (110° C.).

Table III. Effect of Run Time on Conversion with Single Charge of 4,4'-Azo-Bis (4-Cyanopentanoic Acid) (ABCPA) Initiator.

Run No.	Butadiene (g.)	ABCPA (g.)	Pyridine (cc.)	Temp. (°C.)	Time (hr.)	Product Weight (g.)
A33a	5	0.2	15	110	2	1.05
A33b	5	0.2	15	110	5	1.0
A33c	5	0.2	15	110	20	1.0

The problem of initiator exhaustion can be circumvented by incremental addition of the initiator. This procedure is employed very commonly in radical polymerization in which a redox type of initiator is used. The Thiokol Chemical Corporation² has described the use of continuous initiator addition, programmed to maintain a constant ratio of monomer concentration to the square root of initiator concentration, for the preparation of CTPB.

Apparatus and Polymerization Procedure. - Exploratory laboratory runs were carried out in sealed glass ampoules on a five-gram monomer scale with a single charge of initiator. The solvents used in these runs, tetrahydrofuran, dioxane, and pyridine, were chosen so that the polymerizations could be carried out below the solvent boiling point.

Larger scale laboratory runs were made on a 100-gram monomer scale in an autoclave fitted with a liquid injection system to permit incremental addition of the initiator solution. Polymerizations were run at pressures of 300-400 psi. The apparatus consisted of a 300-ml. Amisco (American Instrument Company) shaker vessel equipped with an internal thermocouple and a Lapp injection pump.

The initial pilot plant runs were also carried out on a 100-gram monomer scale. The apparatus consisted of a 300-cc. magnetically stirred autoclave (Autoclave Engineers) equipped with a Lapp pump. In the pilot plant runs, the initiator solution was added continuously and at a constant rate, rather than incrementally. Improvements in procedure adapted in these runs include a smaller pre-reaction initiator charge (3% of the total instead of 10%), a shorter warm-up period (30 minutes instead of 60-70 minutes), and a much decreased cooling period (4 minutes instead of 60 minutes).

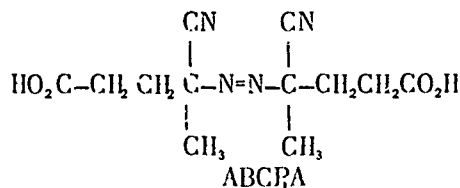
One pound quantities of carboxyl-terminated polybutadiene were prepared in an apparatus consisting of a two-gallon stirred (packed gland) autoclave (Pressure Products Industries; rated 1200 psig at 750° F.) with provisions for heating or cooling in the outside jacket and for cooling through internal coils. A Lapp Pulsafeeder pump was used for feeding the initiator solution continuously.

A diagram of this apparatus is shown in Figure 2 and a detailed description is given in the Experimental Section of the polymerization procedure. This procedure, of course, includes improvements which were made in the course of the work.

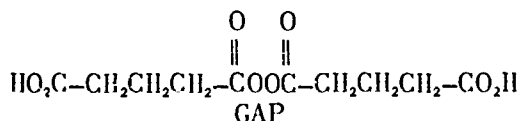
In order to obtain more precise control of the initiator solution addition rate, a Grove back-pressure regulator was introduced so that a constant pressure could be maintained on the outlet of the Lapp pump. A small (30ml.) surge volume was provided ahead of the back-pressure regulator in order to even out the pressure and flow rates. The initiator addition system was further modified so that the initiator solution could be injected through a water-cooled coupling in the bottom of the reactor. This was designed to minimize decomposition of initiator and subsequent coupling to form dibasic acids prior to contact with monomer. Formerly, the addition was made through a dip tube which extended from the top of the reactor through the heated zone and discharged near the bottom of the reactor.

The preparation of CTPB by radical initiation is not a conventional solution polymerization. Initially, it is almost a bulk system, the reactor containing only the (partially liquefied) monomer and a very small amount of solvent and initiator (typically 1850 g. butadiene, 1 g. initiator, and 130 cc. solvent). The main portion of the solvent with the initiator dissolved in it (e.g., 39 g. initiator in 1000 cc. solvent) is added slowly and continuously throughout the reaction period. Even at the end, the solution is still a very concentrated one. Such a system, at 120° C. and 300 psi, might yield 400 grams of polymer in three hours.

Initiators. — Two dicarboxyl-containing radical initiators were investigated extensively in this program. These were 4,4'-azo-bis (4-cyanopentanoic acid) (ABCPA)



and glutaric acid peroxide (GAP).



4,4'-Azo-bis (4-cyanopentanoic acid) (ABCPA) is believed to be the initiator used by the B. F. Goodrich Chemical Company to prepare their carboxyl-terminated polybutadiene (Hycar CTB). This polymer has been found to contain 0.7% nitrogen; the calculated nitrogen content of a polymer of M_{acid} 2300 initiated by ABCPA would be 0.61%.

Also, nitrile groups have been observed in the infrared spectrum of a low molecular weight fraction of the Goodrich polymer. The recent issue of a Dutch patent³ to Goodrich, in which the use of this initiator to obtain carboxyl-terminated polybutadiene is described,

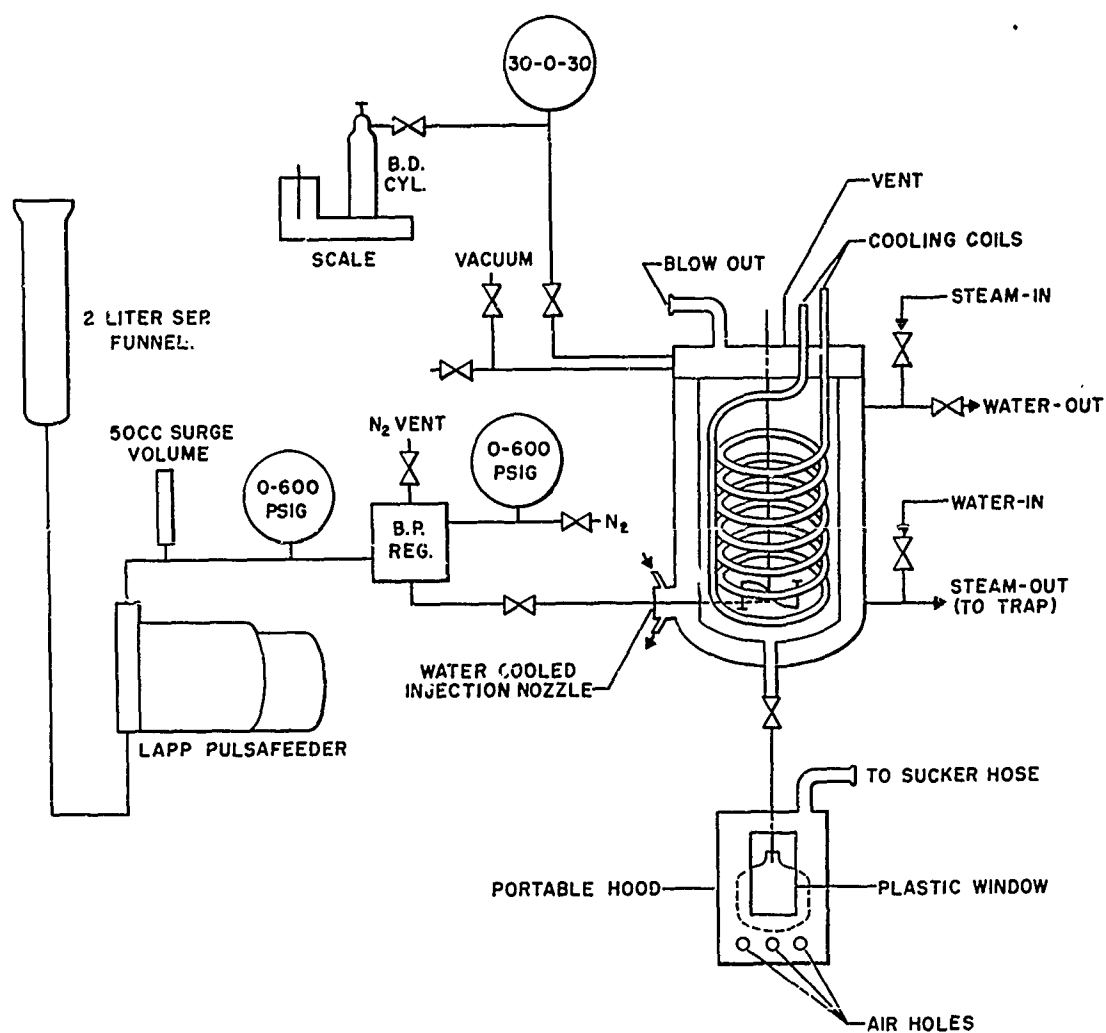
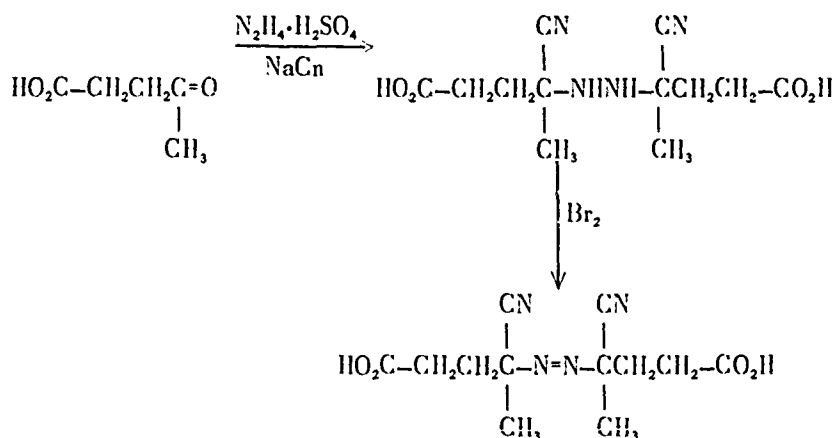


FIGURE 2. Apparatus for Solution Polymerization of Butadiene With Continuous Addition of Initiator.

is also suggestive.

Initial experiments in our laboratory involving ABCPA used initiator prepared according to the procedure of Haines and Waters⁴ by a modified Strecker reaction. Hydrazine sulfate was condensed with levulinic acid in the presence of sodium cyanide- the resulting substituted hydrazine was then oxidized to the azo compound with bromine.



The product of this reaction proved rather tedious to purify, although material of moderately good quality was obtained. Later supplies were obtained from K & K Laboratories, Inc. and then from City Chemical Corporation (130 West 22nd Street, New York 11, New York). Analytical data for the various materials are shown below.

Anal. Calcd. for $\text{C}_{12}\text{H}_{16}\text{O}_4\text{N}_2$: N, 20.0; neutral equiv., 140.

Found for 3M preparation: N, 19.3; neutral equiv., 145.

Found for K & K product: N, 19.9; neutral equiv., 138.

Found for City Chemical product: N, 19.8; neutral equiv., 143.

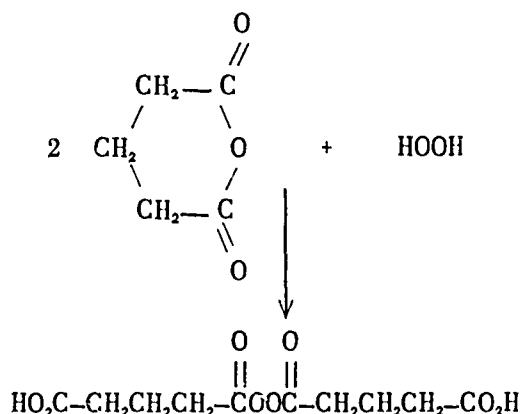
It might be noted that the amount of initiator used to obtain CTPB is substantial, amounting to 10-20% of the weight of carboxyl-terminated polybutadiene produced.

Cavell⁵ who used ABCPA to carry out kinetic studies of the polymerization of acrylamide, has recommended that for such precise investigations the initiator be repurified at frequent intervals. However, in the present work, this was not done, although the initiator was routinely stored under refrigeration.

The use of both succinic acid peroxide and glutaric acid peroxide was investigated in this program. Succinic acid peroxide was obtained from the Lucidol Division of Wallace and Tiernan, Inc. A value of 8.38 milliequivalents iodine per gram was found for the oxidizing power (calculated, 8.55) of this material. The neutral equivalent was determined by potentiometric titration to be 112 (calculated, 117). This compound functioned poorly as an initiator for the polymerization of butadiene, producing very little polymer and most of that crosslinked. Table II in the Appendix shows that conversions were at most 4% to soluble polymer and 7% to crosslinked material.

However, glutaric acid peroxide (GAP) was found quite satisfactory⁶ for the synthesis of CTPB. It is probable that this initiator is used by the Thiokol Chemical Corporation to prepare their carboxyl-terminated polybutadiene (IIC 434), although this cannot be demonstrated by analyses since only $-\text{CH}_2-$ groups are thereby introduced.

Glutaric acid peroxide was prepared from glutaric anhydride and hydrogen peroxide.^{2,7}



In this reaction hydrogen peroxide solution is added to solid glutaric anhydride. Initially a solution is formed, then the product precipitates. No appreciable difference in product quality has been observed when the solid acid anhydride is added to the hydrogen peroxide, rather than the reverse. Even more surprising is the fact that the same product is formed, almost irrespective of the stoichiometry employed. In order to obtain the best yield and quality of product, it has been found important, however, to have good stirring, to maintain a low reaction temperature (about 5° C.), and to avoid the use of very dilute hydrogen peroxide.

The principal impurity found in glutaric acid peroxide is glutaric acid. This material does not interfere with GAP-initiated polymerization, but is carried into the product where it appears, along with the suberic acid formed by the coupling of initiator radicals, as a white sediment which is rather troublesome to remove. Table IV shows analytical data for several samples of the initiator. Most of the large scale initiator preparations have shown oxidizing power values about 95% of the theoretical. In the course of the GAP scale-up work, the practice was adapted of analyzing the glutaric acid peroxide for peroxide content just prior to each polymerization and then making any necessary adjustments to provide exactly the desired charge of active initiator.

Table IV. Analytical Results on Glutaric Acid Peroxide

	Equivalent Weight at 1st Break (two reactive groups)	Equivalent Weight at 2nd Break (three reactive groups)	Peroxide (%)
Calc. for C ₁₀ H ₁₄ O ₈	131	87	12.2
Found for early small prep.	125	80	11.9
Found for early large prep.	122	79	10.9
Found for recent large prep.	—	—	11.6

Solvents. — The requirements for the solvent used in this polymerization are rather demanding, since it must dissolve the monomer, the very polar initiator, and the carboxyl-terminated product. However, it must not itself participate in the polymerization. In most of this work, tetrahydrofuran has been used as the solvent, although

acetone-water and pyridine were also tried. The use of the acetone mixture was described in a patent² issued to the Thiokol Chemical Corporation. However, the initiator was found to have only limited solubility in this medium and there was some tendency for higher molecular weight polymer to appear as a separate phase. Pyridine is also not a very good solvent for the initiator and it is very difficult to remove it completely from the polymer.

Tetrahydrofuran is an excellent solvent for all three components. The possibility that it may act as a chain transfer agent has been of concern, although no evidence has been obtained that this is the case. In fact, a comparison of products obtained in the three solvents (see Figure 3) would indicate that chain transfer is occurring to no greater extent than in the other two systems.

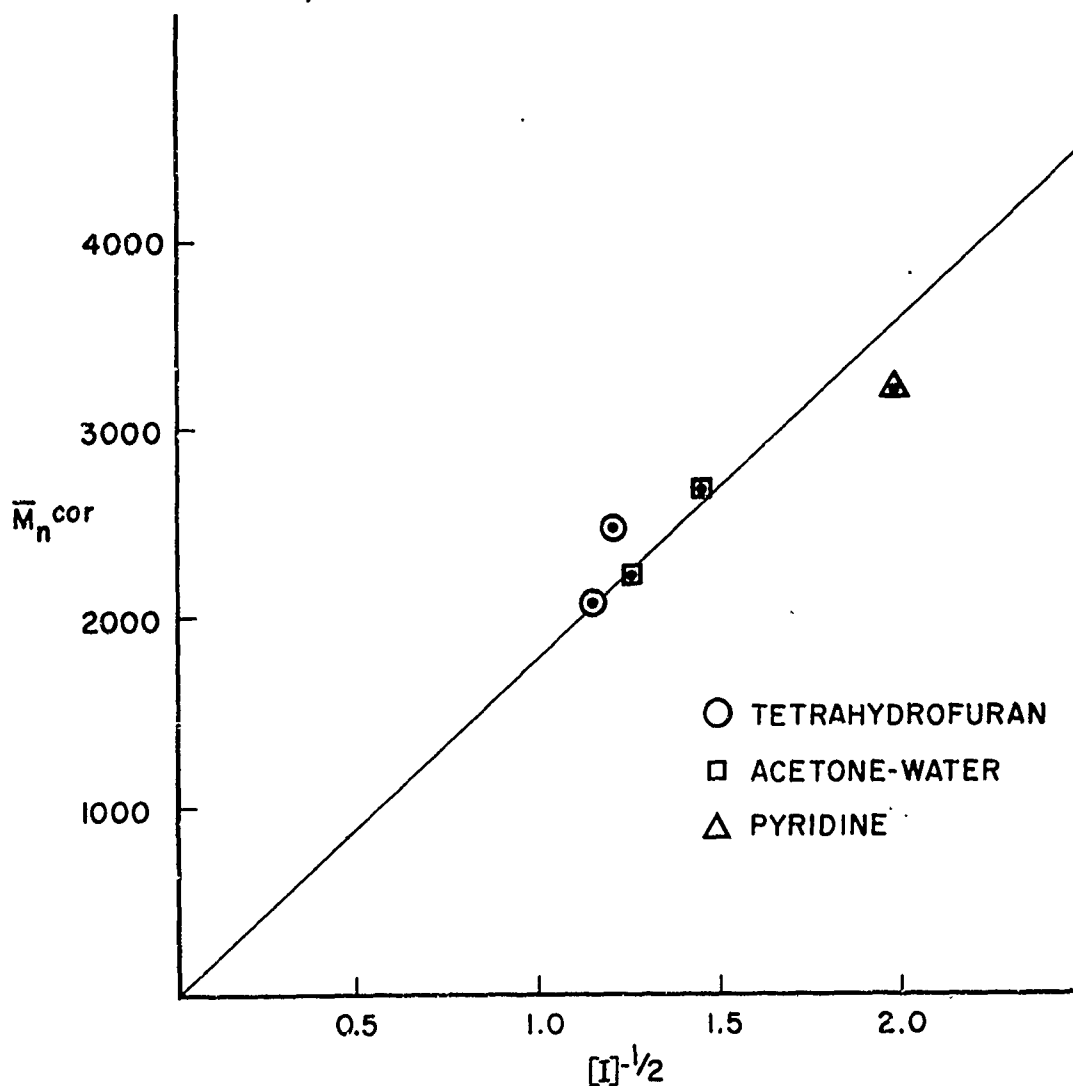


FIGURE 3. Relationship of number-average molecular weight to reciprocal square root of initiator concentration (expressed in g. per increment) for ABCPA-initiated polymerization of butadiene in various solvents.

The use of t-butanol as a solvent for this type of polymerization has been described by the B. F. Goodrich Chemical Company.² The fact that traces of t-butanol were reported by workers at Aerojet³ to be present in CTPB from both Goodrich and Thickol may indicate that this solvent is indeed being used in the commercial preparation of CTPB by radical polymerization.

Tetrahydrofuran is distilled just prior to use to insure that it contains no peroxides. It is not otherwise purified.

Fortuitous Initiation. — Although there was no evidence of polymerization by fortuitous initiator in any of the ampoule runs, some blank runs (monomer, solvent, no initiator) in the scale-up equipment gave as much as 9% polymer. This fortuitous initiation was at first thought to be due exclusively to oxygen dissolved in the solvent. And indeed, fortuitous polymerization was virtually eliminated (0.6%) when the solvent was degassed by three freeze-pump-thaw cycles with subsequent storage under nitrogen. However, it now appears probable that the reaction vessel itself contained contaminants which could act as initiators. These appear to have been consumed after two or three runs, and in a well-used reactor, blank runs with non-degassed solvent generally yielded only 2% polymer.

The polymer (Table V, Runs A48 and B18) produced by fortuitous initiation is, of course, non-carboxyl-terminated. It has an exceptionally broad molecular weight distribution (\bar{M}_w/\bar{M}_n , 5.7 for 9% conversion, 19.6 for 3% conversion).

The first 100-gram acetone-water run also appeared to contain fortuitous polymer (Run A36; functionality, 1.4; \bar{M}_w/\bar{M}_n , 11.9). The second run also contained such material, although to a lesser extent. A portion of this product precipitated out of the aqueous acetone solution. Initially, it appeared to be desirable polymer (Run A37i; \bar{M}_n 3650; functionality, 2.1). However, it was later found to have a very broad molecular weight distribution (\bar{M}_w/\bar{M}_n , 6.7) without the much increased functionality one would expect of highly branched CTPB.

In the large stirred autoclave it was found that a small amount of crosslinked polymer was formed which tended to collect on the walls of the reactor. The reactor was opened every five or six runs and this material, which was somewhat like crepe paper, was removed. It amounted to about 0.2-3% conversion per run.

Work-up Procedure for Azo-Initiated CTPB. — The one-pound azo-initiated polymers were worked up by stripping the tetrahydrofuran at 60° C. under vacuum (after addition of the antioxidant) and then dissolving in benzene, filtering, and evaporating the filtered solution to dryness in a rotary evaporator at 60°C. under vacuum.

A later section of this report describes difficulties experienced in removing coupled radicals from the peroxide-initiated polymer. In the azo-initiated polymerization, this was not a serious problem. A material believed to be the analogous coupled product was obtained in this system, but it was insoluble in benzene and was easily removed by filtration.

In the higher molecular weight runs (\bar{M}_n 4500-5000) relatively little of this insoluble material was formed. In the lower molecular weight runs (\bar{M}_n 1500-3000) the amount of insoluble residue removed by filtration was increased. One should bear in mind that in the latter runs four times as much initiator was used as in the former. This sediment, a grayish-white solid, is obviously derived from the initiator. Its infrared spectrum indicates that initiator itself is not a major component. The spectrum does show -CN groups and -CO₂H absorption, however,

TABLE V A. FORTUITOUS INITIATION

Blank Runs and Early Autoclave Runs

Run No.	BD (g.)	ABCPA (g.)	Solvent (cc.)	No. of Aliquots	Aliquot Conc. (g./aliquot)	Degassed	Time to Bring to Temp. (hrs.)	Addition Time (hrs.)	Post-Heating (hrs.)	Temp. (°C.)	Conv. (%)	Calco 2246 (%)
A48	96	None	100 Acetone	21.5	0.000	No	1:10	2:05	0:00	115-120	9	2.2
B6	96	None	148:5.4 Acetone -H ₂ O	18	0.00	Yes				115-121	0.6	
B18	95	None	95 Tetrahydrofuran	13.5	0.00	No	1:00	1:05	0:30	113-121	2.6	9.0
A36	92	10	82:4.6 Acetone -H ₂ O	22	0.455	No	1:20	2:15	0:20	106-123	Not Available	7.0
A37	92	10	82:4.6 Acetone -H ₂ O	22	0.455	No	1:20	2:15	0:20	116-122	i, 12 s, 41	1.3 2.1

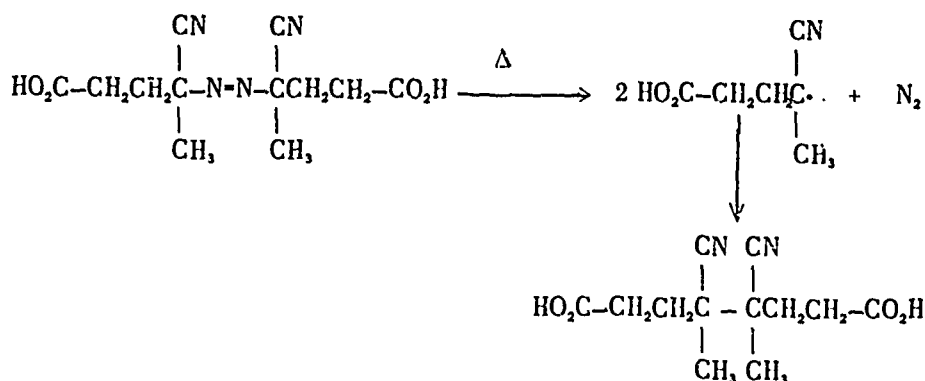
TABLE V B. FORTUITOUS INITIATION

Blank Runs and Early Autoclave Runs

Run No.	Equiv. Wt. per Carboxyl, \bar{M}_{acid}	\bar{M}_n^{obs}	\bar{M}_n^{cor}	Functionality, \bar{M}_n/\bar{M}_{acid}	$\langle \eta \rangle$ (1% in C ₆ H ₆)	\bar{M}_v	\bar{M}_v/\bar{M}_n	Comments
A48	--	2400	2780	--	.30	16,200	5.8	Fortuitous polymer (blank run)
B18	--	1340	1890	--	.57	37,000	19.6	Fortuitous polymer (blank run)
A36	2245	1990	3135	1.4	.58	38,000	12.4	Considerable fortuitous polymer
A37i	1731	3240	3650	2.1	.41	24,000	6.6	Pptd. phase; some fortuitous polymer
A37s	220	1600	1740	2.4	.11	4,500	2.6	Soluble phase

i, precipitated phase; s, soluble phase

and this material probably consists for the most part of the coupled product.



The azo-initiated polymer was subjected to water washing to see how much polymer would thus be removed. Batch 12 (a probing run; Table XI) was used for these studies. It was worked up in the normal way and then subjected to two water washes. The resulting product was further washed four more times with water and then another four times. During this treatment the acid equivalent weight increased from 1600 to 1735 to 1800.

Dry weights and acid equivalent weights were determined on aliquot portions of washes 3-8. Results are shown in Table VI.

Table VI. Water-Washing of Azo-Initiated CTPB.

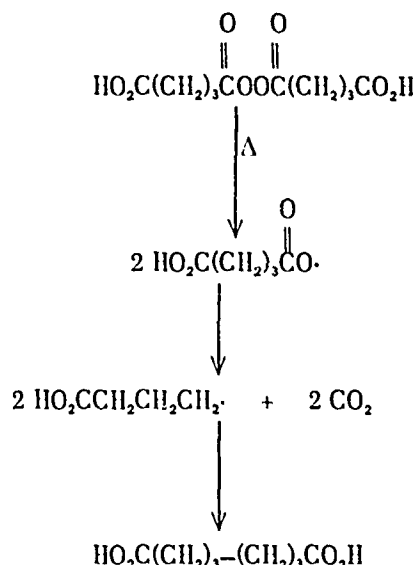
Treatment	Acid Equiv. Wt. of Polymer (M_{acid})	Analysis of Water-Soluble Material	
		Percent by wt. of polymer	Acid Equiv. Wt.
After 2 washes	1600		
3rd wash		1.0	338
4th wash		0.4	323
5th wash		0.3	417
6th wash	1735	0.2	260
7th wash		0.2	333
8th wash		0.1	454
9th wash		—	—
10th wash	1800	—	—

The acid equivalent weight of the material removed by water-washing was always higher than that of coupled initiator (140). This indicates that low molecular weight polymer was being removed. This was further shown by the fact that the residues obtained by evaporating the water washes to dryness were sticky liquids.

Work-up Procedure for Peroxide-Initiated Polymer. — The crude product remaining after the tetrahydrofuran solvent has been stripped from GAP-initiated CTPB is noticeably contaminated with a white solid. This material is not removed by dissolving the polymer in benzene, filtering, and then evaporating the filtrate to dryness. The benzene-treated polymer initially appears cloudy; upon standing or storage in the refrigerator it tends once again to form the white precipitate.

This solid is essentially free of residual initiator. Furthermore, a potassium iodide test of a water wash of the crude polymer showed only the faintest trace of peroxide activity.

The solid has been found (IR) to consist principally of suberic acid, with glutaric acid sometimes present also. Suberic acid is, of course, formed by the coupling of initiator radicals.



No ester linkages were detected by infrared spectroscopy in the precipitate. This suggests that all of the carbon dioxide is lost before any coupling takes place. Glutaric acid is not found in all runs; it appears to be present in some samples of initiator and to be carried through the polymerization.

The production of radical-initiated polymer by 3M has two major concerns:

- 1) Reproducibility of the procedure.
- 2) Suitability of the product for propellant use.

As far as reproducibility is concerned, the removal of suberic and glutaric acids would not be of concern provided the same amounts were always present. From a propellant point of view, it is probably undesirable to have these acids present. Although they are difunctional and fully able to participate in network formation; the resulting structure would be tighter than required unless a difunctional curative were incorporated into the curative. This would likewise be the case for very low molecular weight polymer.

When it was realized that benzene-extraction was not satisfactory for the separation of GAP-initiated polymer from coupled initiator, alternative purification procedures were investigated. In the small scale laboratory runs, the polymers were worked up by filtration of their cyclohexane-benzene solutions. A 3:1 (by volume) cyclohexane-benzene mixture was found most satisfactory. These polymer samples were not, in general, stored under refrigeration, and it is possible that this procedure was not indeed adequate to insure the complete removal of initiator residues.

In the pilot plant, purification was initially attempted by water-washing. This is one of the work-up procedures described in a patent issued to the Thiokol Chemical Corporation? Thiokol is believed actually to be using this process to purify HC-434. This polymer was found to contain about 80 ppm sodium, apparently introduced by the washwater.

The Thiokol procedure involves washing the neat polymer. This may be satisfactory on a very large scale, but it was our experience that it resulted in considerable mechanical losses of polymer. Accordingly, the pilot plant peroxide-initiated polymers were dissolved in benzene and then washed. The products thus obtained were initially clear; however, they were all found to contain precipitated solid after standing in the refrigerator.

It is important to note that water washing removes some low molecular weight polymer and therefore has to be very carefully controlled if a reproducible product is to be obtained. The marked effect of this treatment on the acid equivalent of peroxide-initiated polymers is shown in Table VII. Polymer which has been washed always shows the higher equivalent weight (less low molecular weight acid-containing material).

It was eventually found in the case of the low molecular weight peroxide-initiated polymer that a clear product could be obtained by dissolving the crude polymer in cyclohexane, filtering, stripping off about three-fourths of the solvent, filtering again, and then evaporating completely to dryness. The polymer obtained by this procedure remained clear on storage under refrigeration.

In general, 30-35 g. of solid was removed in the first filtration, 5-10 g. in the second of the low molecular weight polymers. Analysis by infrared spectroscopy and titration with base of the solid obtained in one run (Run 37; Table XIV) indicated it to be about 85% succinic acid and 15% glutaric acid.

It was found that the higher molecular weight peroxide-initiated polymers could be purified by extracting a carbon tetrachloride solution of the polymer with isopropanol followed by removal of the carbon tetrachloride.

TABLE VII. EFFECT OF WASHING ON ANALYTICAL RESULTS FOR PEROXIDE-INITIATED CTPB.

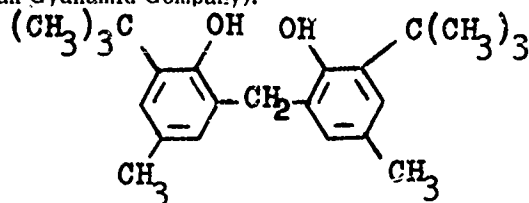
	% Calco Found	$\langle \eta \rangle$ (1% in C_6H_6)	\bar{M}_v	\bar{M}_{acid}	\bar{M}_v/\bar{M}_{acid}
Run 25					
After two water washes	2.6	.25	12,800	2380	5.4
After four water washes	2.6	.25	12,800	2620	4.9
Run 26					
After water washing		.26	13,500	2420	5.6
With subsequent aqueous isopropanol washing		.26	13,500	2790	4.8
Run 27					
After water washing		.28	14,900	2420	6.2
With subsequent aqueous isopropanol washing		.27	14,200	3170	4.5
Run 29					
After water washing		.24	12,200	2190	5.6
With subsequent aqueous isopropanol washing		.23	11,500	2650	3

Antioxidants. — In general, Antioxidant 2246, at levels of 1-2% was used to stabilize the polymers. In a few cases, antioxidants supplied by NOTS were used.

It was thought advisable to determine the molecular weight by vapor phase osmometry of Antioxidant 2246. This was a check on the validity of using calculated molecular

weights to correct the number-average molecular weight of polymers for their antioxidant content. Actually, one has no assurance that the antioxidant in an aging polymer sample still has its original molecular weight (antioxidants can undergo profound changes in the performance of their function), but no better estimate of the operating value is easily available.

A molecular weight of 350 was found for Antioxidant 2246 (also known as Calco 2246, supplies by the American Cyanamid Company).



Antioxidant 2246 or Calco 2246

The calculated value is 340.

Effect of Initiator Concentration on Molecular Weight. — A major goal of this program has been to demonstrate an ability to control the molecular weight of carboxyl-terminated polybutadiene, prepared with the two different radical initiators. Consequently, considerable effort has been expended on the study of the experimental factors affecting molecular weight. In this regard, initiator concentration has been of primary interest.

Investigations were carried out in the laboratory in the ABCPA-initiated system in some detail. The GAP-initiated polymerization was also studied, although to a lesser extent, because the principles learned in working with the azo initiator could for the most part be applied to the peroxide case as well.

According to the simplest kinetic scheme for an addition polymerization proceeding via a radical mechanism, the number-average molecular weight should be related to (M) , the monomer concentration, and to (I) the initiator concentration, as shown:

$$\bar{M}_n \sim \frac{(M)}{(I)^{1/2}}$$

In the system used for CTPB preparation, in which the initiator is added constantly in order to maintain a continuing supply of radicals, care must be taken to use a meaningful initiator concentration. Valid comparisons between runs appear to be possible on the basis of weight of initiator added per unit time per total accumulated volume of solution.

The effect of initiator concentration on molecular weight was first examined for ABCPA-initiated polymerizations. Table VIII shows data for several runs carried out in the laboratory autoclave at $117^\circ (\pm 5^\circ \text{C.})$ with approximately equal monomer charges. The initiator solution was added incrementally at 6-minute intervals. Other experimental conditions were deliberately varied. Thus, three different solvent systems were used, i.e., acetone-water, pyridine, and tetrahydrofuran. The total amount of initiator was varied from 3 to 10 parts per hundred parts of monomer, the total addition period from 40 minutes to 100 minutes, and conversions from 21% to 51%. Figure 3 shows a plot of number-average molecular weight against the reciprocal of the square root of the initiator concentration for these runs. The predicted linear dependence was obtained.

Another series of runs was made with all variables held constant except the concentration of initiator (Table IX). Various amounts of ABCPA initiator were dissolved in acetone-water (92:8 by weight) and the resulting solution added in 6-cc. increments every 6 minutes. Figure 4 shows a plot of \bar{M}_{acid} , the equivalent weight per carboxyl group, against $(I)^{-1/2}$. Figure 5 shows a plot of the viscosity-average molecular weight against $(I)^{-1/2}$. The anticipated straight line relationship was obtained in both cases. The equivalent weight per carboxyl group is in some ways a more fundamental characteristic for radical-initiated CTPB than either of the other molecular weight averages, since the latter are affected by branching, while the former is not. In fact, if one assumes that all ends are carboxyls, the equivalent weight is equal to the kinetic chain length of the reaction multiplied by the molecular weight of a monomer unit. The kinetic chain length, of course, is simply a count of the average number of propagation reactions occurring per initiation.

TABLE VII A. FREE RADICAL POLYMERIZATIONS
ABCPA - INITIATED RUNS IN VARIOUS SOLVENTS IN LABORATORY AUTOCLAVE

Run No	BD (g.)	ABCPA (g.)	Solvent (cc.)	No. of Aliquots	Aliquot Conc. (g./aliquot)	Time to Bring to Temp. (hr.)	Addition Time (hr.)	Post-Heating (hr.)	Temp. (°C.)	Conv. (%)	Calco 2246 (%)
A47	100	10.4	103:7.7 Acetone-H ₂ O	18.5	0.562	1:00	2:05	0:00	100-112	49	1.9
A51	96	8.4	56:2.0 Acetone-H ₂ O	13.5	0.622	1:10	1:05	0:20	115-120	26	6.2
A52	96	8.4	74:2.7 Acetone-H ₂ O	18	0.467	0:50	1:35	0:30	115-120	33	6.2
B2	95	2.4	55 Pyridine	9.5	0.253	0:40	0:40	0:40	112-120	21	7.8
B4	100	10.4	80 Tetrahydrofuran	15	0.693	1:20	1:10	0:50	115-121	37	3.2

TABLE VIII B. FREE RADICAL POLYMERIZATIONS
ABCPA-Initiation Runs in Various Solvents in Laboratory Autoclave

Run No.	[I]	[I] ^{-1/2}	\bar{M}_{acid}	\bar{M}_n^{obs}	\bar{M}_n^{cor}	\bar{M}_n/\bar{M}_{acid}	$\langle \eta \rangle$ (1% in C ₆ H ₆)	\bar{M}_v	\bar{M}_v/\bar{M}_{acid}
A47	0.562	1.33	810	1910	2100	2.6	.12	5,000	6.2
A51	0.622	1.27	980	1670	2250	2.3	.14	6,100	6.2
A52	0.467	1.46	1030	2030	2750	2.7	.15	6,700	6.5
B2	0.253	1.99	1370	1880	3050	2.2	.20	9,700	7.1
B4	0.693	1.20	1080	2080	2505	2.3	.16	7,200	6.7

TABLE IX A. FREE RADICAL POLYMERIZATIONS

Laboratory Autoclave Runs with Varying Amounts of ABCPA^a

Run No.	ABCPA (g.)	No. of Aliquots	Time to Bring to Temp. (hrs.)	Addition Time (hrs.)	Post Heating (hrs.)	Temp. (°C.)	Conversion (%)
B20	1.0	16.5	1:00	1:25	0:30	114-120	7
B14	4.0	16.5	1:00	1:25	0:30	114-120	25
B19	4.0	15.5	1:00	1:20	0:30	115-121	29
B11	6.0	16.5	1:05	1:25	0:30	114-121	31
B12	8.0	18.5	1:00	1:30	0:30	114-121	50
B19	8.0	16.5	1:10	1:25	0:30	112-120	40
B13	12.0	17.5	1:10	1:30	0:30	114-122	67

^a Initiator was dissolved in mixture of 120 cc. acetone and 8 cc. water; butadiene charge 80 g. in each run.

TABLE IX B. FREE RADICAL POLYMERIZATIONS

Laboratory Autoclave Runs with Varying Amounts of ABCPA

Run No.	Conc. of Initiator, [I] (g. per aliquot)	$[I]^{-1/2}$	\bar{M}_{acid}	$\langle \eta \rangle$ (1% in C ₆ H ₆)	\bar{M}_v	\bar{M}_v/\bar{M}_{acid}
B20	.061	4.0	2470	.26	13,500	5.5
B14	.242	2.0	1260	.16	7,200	5.7
B10	.258	2.0	1410	.17	7,800	5.5
B11	.364	1.7	1160	.17	7,800	6.7
B12	.432	1.5	1150	.15	6,700	5.8
B19	.485	1.4	980	.14	6,100	6.2
B13	.615	1.3	990	.15	6,700	6.8

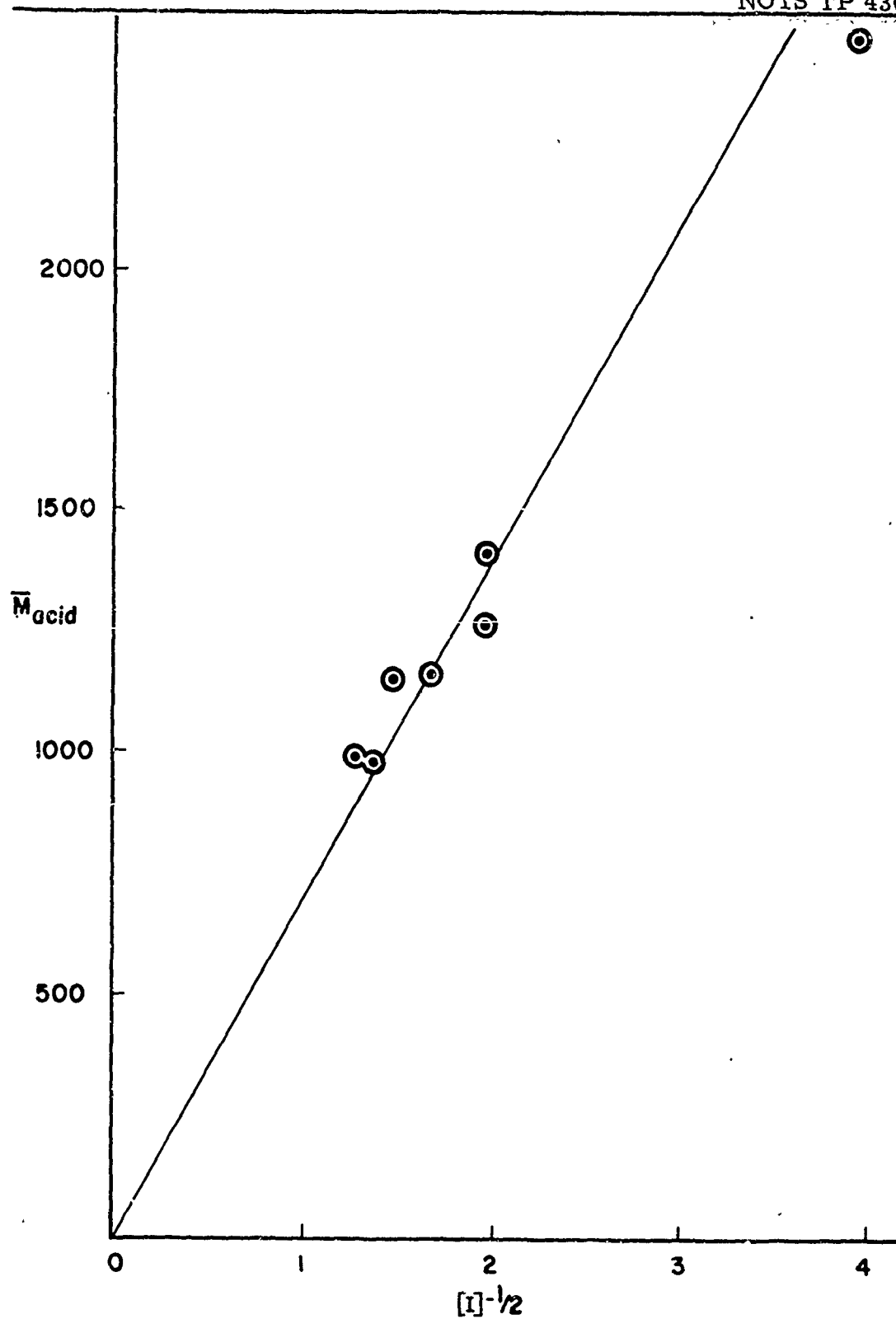


FIGURE 4. Relationship of equivalent weight (\bar{M}_{acid}) of ABCPA - initiated CTPB to reciprocal square root of initiator concentration (expressed in g. per increment added).

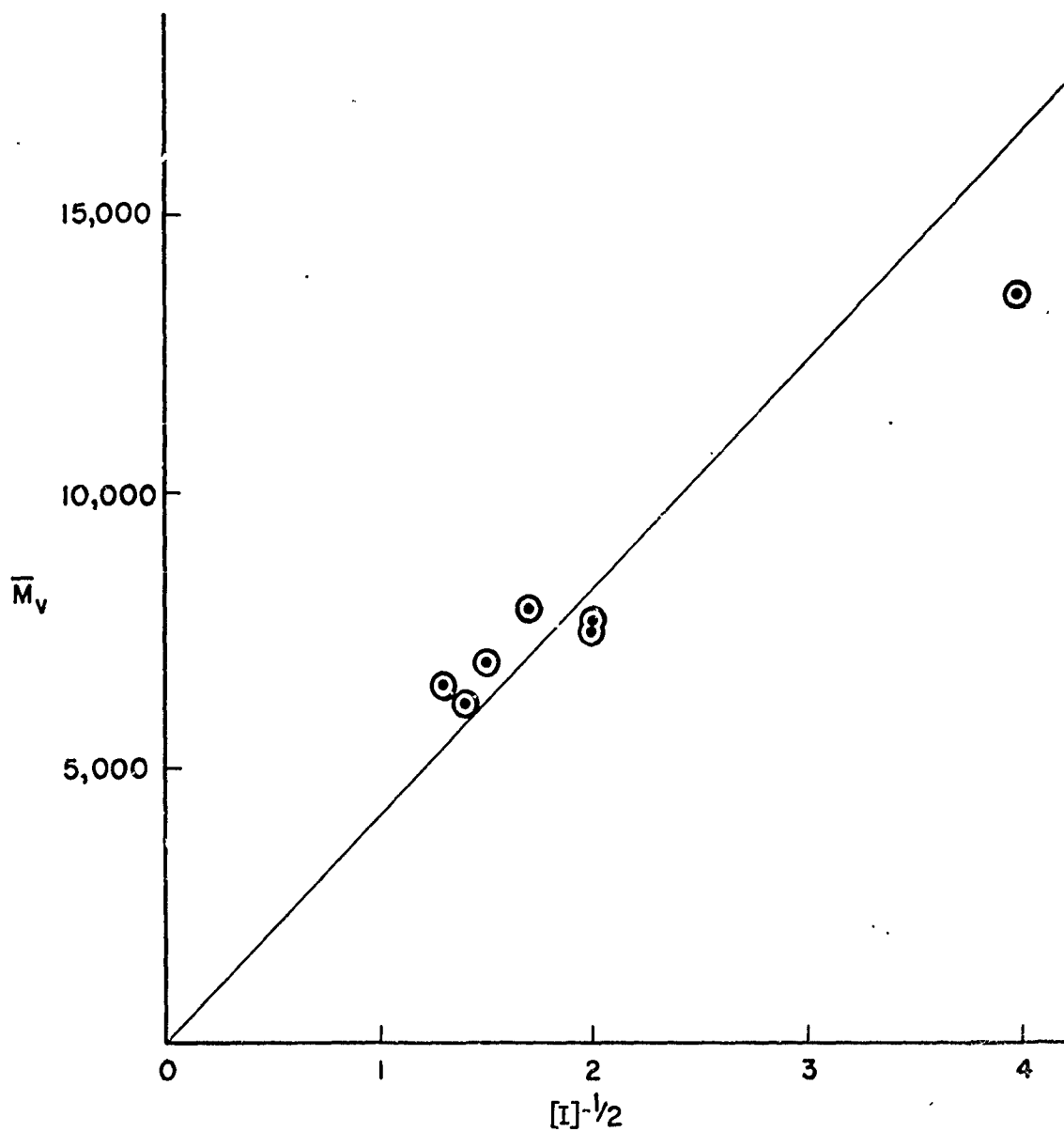


FIGURE 5. Relationship of viscosity-average molecular weight of ABCPA — initiated CTPB to reciprocal square root of initiator concentration (expressed in g. per increment added).

The GAP-initiated polymerization of butadiene also shows an inverse relationship of molecular weight to the square root of initiator concentration. Some results for ampoule runs are shown in Figure 6. The data for these runs are given in Table III in the Appendix.

Conversion. — Simple kinetics would predict that the rate R_p of production of polymer (at any instant) would be proportional to the monomer concentration and to the square root of the initiator concentration.

$$R_p \sim (M) (I)^{1/2}$$

In Table IX are shown data for a series of runs in which all conditions were essentially duplicated except the initiator content per increment. The run time was the same in all cases. Figure 7 shows a plot of conversion against $(I)^{1/2}$ for these runs.

If all the initiator added in one increment were exhausted before the next addition, the initiator concentration in any one run could be treated as a constant. One would then expect to have a negative curvature in the plot of conversion versus $(I)^{1/2}$, since the decrease in monomer concentration is greater in a high conversion run than in a low conversion one. The fact that a positive curvature has been obtained probably indicates that initiator is gradually accumulating in the system. It should be noted that conversions as high as 74% have been obtained by means of the incremental addition procedure. The reaction could, no doubt, be carried as close to 100% as appeared desirable.

Molecular Weight and Conversion in Pilot Plant Runs. — On the basis of the laboratory experiments, work was begun in the pilot plant on the production of one-pound lots of both azo- and peroxide-initiated polymer at number-average molecular weights of about 2500 and about 5000. At this point, it became important to consider the yield of polymer, as well as its molecular weight, and to attempt to avoid unnecessary losses of initiator (ABCPA initiator, especially, tended to be in short supply).

In the pilot plant a standard or "base-line" procedure was first established for runs carried out on a 100-gram monomer scale in a 300-ml. stirred reactor with continuous addition of ABCPA-initiator. Good reproducibility was achieved. The data for five successive similar runs are shown in Table X. This procedure produced polymer of \bar{M}_{acid} about 850 in conversions of about 50%. Corrected number-average molecular weights varied from 1600 to 2185 (four of the five runs were between 1600 and 1725) and inherent viscosities from .09 to .11. Throughout the course of this work, base-line runs were made periodically to insure that reproducibility was continuing to be achieved. Blank runs (no initiator) were also carried out frequently.

Table XI shows the large number of runs which were carried out in this reactor to serve as a basis for scale-up to the two-gallon-reactor. Results of a few of these are singled out to illustrate general principles.

In Runs 27 and 28, the quantity of initiator was reduced to 38% of the base-line amount. This was added in the standard period of time with the standard amounts of butadiene and tetrahydrofuran. As expected, the acid equivalent (and hence the molecular weight) was increased by a factor of about 1.6.

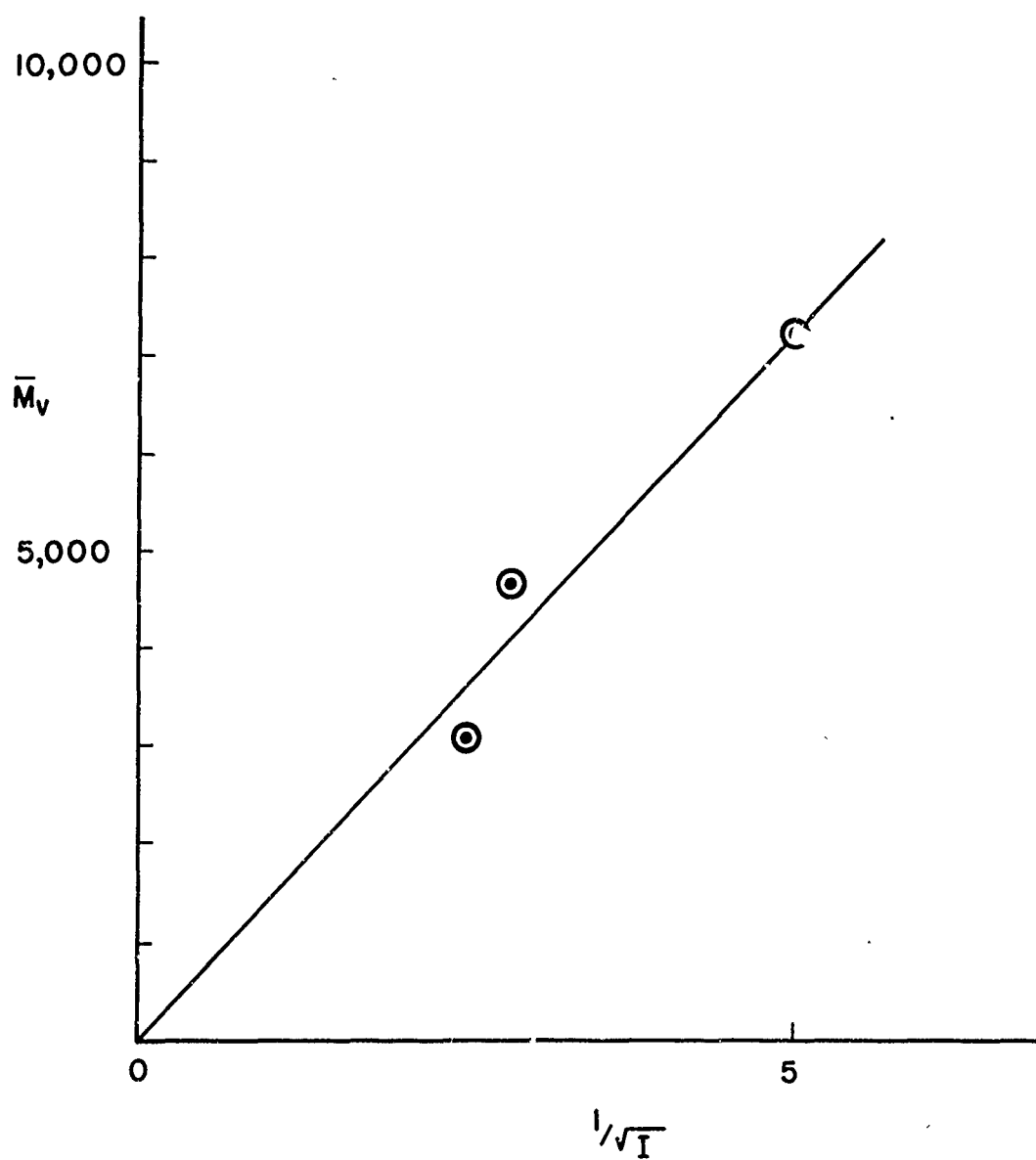


FIGURE 6. Relationship of viscosity-average molecular weight of GAP-initiated CTPB to reciprocal square root of initial initiator concentration (expressed in g. added).

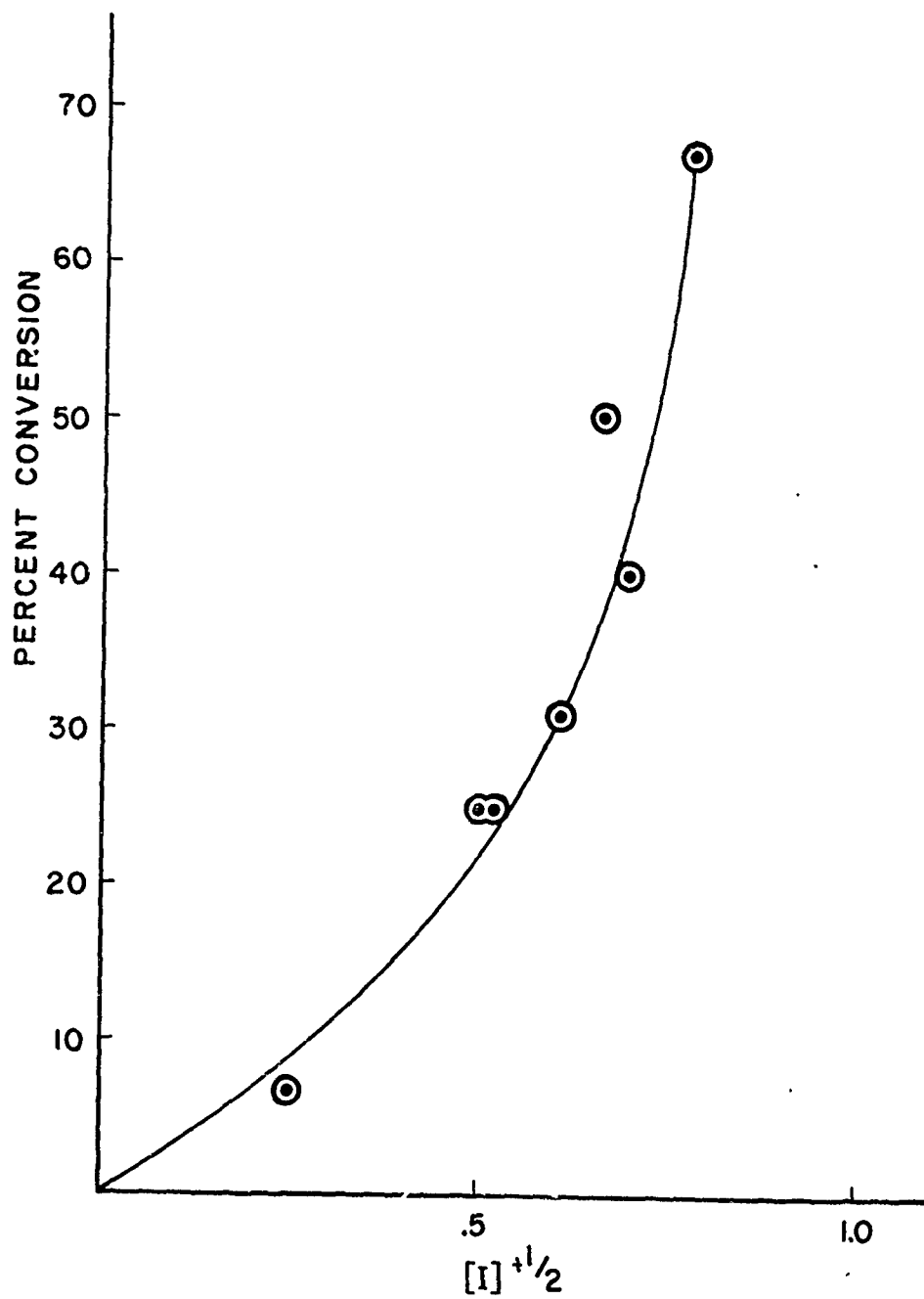


FIGURE 7. Total conversion as a function of square root of initiator concentration in polymerization of butadiene with ABCPA added in equal increments.

$$\bar{M}_{\text{acid}} = 850$$

$$\frac{\bar{M}'_{\text{acid}}}{\bar{M}_{\text{acid}}} = \frac{(I)^{1/2}}{(I')^{1/2}}$$

$$\frac{\bar{M}'_{\text{acid}}}{850} = \left(\frac{1}{.38} \right)^{1/2} = 1.6$$

$$\bar{M}'_{\text{acid}} (\text{predicted}) = 1.6 \times 850 = 1360$$

$$\bar{M}'_{\text{acid}} (\text{obtained}) = 1400$$

In this process, however, the conversion was cut from about 50% to 24%. This, too, was anticipated from the laboratory experiments.

TABLE X. FREE RADICAL POLYMERIZATIONS

Pilot Plant "Base-Line" Runs in 300-Ml. Reactor with ABCPA Added Continuously^a

Run No. (Notebook 18554)	\bar{M}_{acid}	\bar{M}_n^{obs}	\bar{M}_n^{cor}	Conv. (%)	Func. ($\bar{M}_n/\bar{M}_{\text{acid}}$)	$\langle \eta \rangle$ (1% in C_6H_6)	\bar{M}_v	$\bar{M}_v/\bar{M}_{\text{acid}}$
8	820	1650	1725	50	2.1	.11	4500	5.5
9	845	1510	1600	49	1.9	.10	4000	4.8
	840	1520	1625		1.9	.10	4000	4.7
10	850	1650	1705	43	2.0	.09	3500	4.1
11	925	1540	1620	52	1.8	.11	4500	4.9
12	960	2020	2185	47	2.3	.09	3500	3.8

^aAll runs were carried out at 120°C. with an initial charge of close to 100 g. of butadiene and 10 cc. of tetrahydrofuran. The initiator solution, approximately 9.6 g. of ABCPA diluted to 100 cc. with tetrahydrofuran, was added continuously over a 1-hour period.

TABLE XI A. FREE RADICAL POLYMERIZATIONS

Pilot Plant ABCPA-Initiated Runs in 300-ml. Reactor

Run No.	Run Type	BD ^a (g.)	ABCPA ^b (total g.)	THF ^c c' + c'' (ml.)	Time to Reaction Temp. (hr.)	Reaction Temp. (°C.)	Addn. ^d Time (hr.)	Time to Discharge (hr.)	Discharge Temp. (°C.)	Discharge Time (hr.)	Mat'l. Balance ^e (wt. %)	Polymer (g.)	Comments
1	Blank ^h	89.5	0	80	1:00	120	1:10	0:05	-10			0.2	15 ml. THF added at 10° THF feed inoperative
2		91	0										
3	Probing Runs	91.6	0	84.5	0:40	120	1:00	0:04	5			<0.2	Stirrer trouble Temp. controller & stirrer trouble
4		94	5.2 ^j	40	0:33	120	1:15	0:08	20			26	
5		98.6	8 ^j	60	0:27	118-123	1:10	0:14	-10			45.5	
6		88.3	10 ^j	70	0:25	120	1:30	0:20			97	41.8	
7		93.4	10 ^j	70	0:30	120	2:12	0:05	-10		>90	42.3	Stirrer trouble
8		93.4	10.4 ^j	80+50	0:23	120	1:00	0:07	-10	0:10	94	47.0	Stirrer trouble
9		103.7	10 ^j	70+50	0:23	120	1:00	0:05	-5	0:47	96	50.4	Stirrer trouble, addn. trouble.
10	Base line	101.7	9.6 ^j	100+10	0:24	120	0:59	0:04	-10	1:30	97	43.6	Stirrer trouble
11		92.3	9.6 ^j	100+10	0:25	120	1:00	0:04	-10	0:33	97	47.8	Stirrer trouble
12		105.4	9.6 ^j	100+10	0:25	120	1:00	0:05	-10	0:33	90	49.8	Stirrer trouble
13	Blank	97.0	0	100+10	0:27	120	1:00	0:03	-10	0:37	98	2.0	Leaky THF feed valve
14	Base line	91.9	9.6 ^j	100+10	0:28	120							
15		101.7	9.6 ^j	100+10	0:32	120	1:00	0:03	-10	1:05	94	50.2	Stirrer trouble Temp. controller & stirrer trouble
16	Lower temp.	97.8	9.6 ^j	100+10	0:21	100	1:00	0:03	-10	1:47	96	31.1	
17		96.4	9.6 ^j	100+10	0:20	100	1:00	0:03	-10	1:42	94	28.3	
18		95.1	9.6 ^j	100+10	0:20	100	1:00	0:03	-10	2:07	96	30.7	
19	Short time	94.8	4.8 ^j	50+10	0:28	120	0:29	0:03	-10	1:38	97	22.1	
20	Blank	95.5	0	100+10	0:25	120	1:00	0:04	-10	0:16	98	2.9	
21	Base line	94.8	9.6 ^j	100+10	0:26	120	1:00	0:04	-10	1:08	92	48.6	
22	Short	96.1	4.8 ^j	50+10	0:28	120	0:39	0:04	-10	0:39	93	19.0	
23	time	94.8	4.8 ^j	50+10	0:29	120	0:32	0:03	50	0:30	94	19.0	
24	No pre-addn.	94.4	9.6	100+10	0:30	120	1:00	0:07	60	1:13	94	43.8	
25	of	94.1	9.6	100+10	0:25	120	1:00	0:01	75	1:12	93	46.6	
26	initiator	95.3	9.6	100+10	0:30	120	1:00	0:01	55	1:09	95	48.4	
27	Lower	93.4	2.6 ^j	100+10	0:27	120	1:00	0:02	55	1:30	94	21.1	
28	initiator	93.1	2.6 ^j	100+10	0:32	120	1:00	0:02	60	1:00	96	22.7	
29	Blank	93.8	0	100+10	0:26	120	1:00	0:02	50	1:13	96	1.7	
30	Base line	95.1	9.6 ^j	100+10	0:23	120	1:00	0:02	50	1:00	92	49.8	
31	Lower init.	95.1	5.2 ^j	100+10	0:27	120	2:00	0:02	50	0:58	97	46.1	
32	longer time	96.1	5.2 ^j	100+10	0:25	120	2:00	0:02	50	0:58	99	51.0	
33	Pre-reaction	94.5	0.3 ^j	3+10	0:25	120	0	0:01	50	0:53	97	1.8	
34	initiator only	95.1	0.3 ^j	3+10	0:23	120	1:00	0:01	50	1:08	99	2.8	

^aBD = butadiene; ^bABCPA = 4, 4'-azo-bis (4-cyanopentanoic acid); ^cTHF = tetrahydrofuran, freshly-distilled; ^{c'}Total volume of initiator solution in THF; ^{c''}Volume of pure THF charged prior to BD addition; ^dOf THF solution of ABCPA; ^eOf total weight of BD, THF, and ABCPA charged; ^fWt. % of Calco in polymer; ^gDetermined by UV; ^hblank, i.e. no initiator added; ⁱBase line, i.e. arbitrarily selected standard set of conditions; ^j3 ml. of initiator solution added at room temp. just before heating was begun; ^kPurified by evaporating to dryness, dissolving in benzene, filtering benzene solution, and again evaporating to dryness.

TABLE XI B. FREE RADICAL POLYMERIZATIONS

Pilot Plant ABCPA-Initiated Runs in 300-Ml. Reactor

Run No.	Run Type	Antioxidant 2246 (g.)	(% Chgd.)	(% Found) ¹	$\langle \eta \rangle$ (1% in C ₆ H ₆)	\bar{M}_{acid} IR Peak Ht.	Titration	\bar{M}_n^{obs}	\bar{M}_n^{cor}	$(\bar{M}_n/\bar{M}_{acid})$	Infrared Analysis (% cis. trans, vinyl)
1	Blank ^h										
2											
3											
4	Probing runs	2.1			.14	0.525	980	2110	2375	2.4	18,43,29
5					.12		980				
6		0.7	1.7		.12		1320				
7		0.8	1.9		.15		1220				
8	Base ⁱ line	0.8	1.7	1.1	.11		820	1650	1725	2.1	
9		0.8	1.6	1.6	.10		845	1510	1600	1.9	
10		0.8	1.8	1.8	.10	0.526	840	1520	1625	1.9	
11		0.8	1.7	0.8	.09		850	1650	1705	2.0	17,42,27
12		0.8	1.7	1.4	.11		925	1540	1620	1.8	
13		0.8	1.6	1.5	.09		960	2020	2185	2.3	
14	Blank										
15	Base line	0.8	1.6		.11						
16	Lower temp.	0.8	2.6		.08						
17		0.8	2.8	2.8	.09	0.694	590 ^k				13,39,24
18		0.8	2.6	2.7	.07	0.719	590 ^k				13,40,25
19	Short time	0.8	3.6		.12						
20	Blank	0.2	6.9								
21	Base line	0.8	1.6	1.9	.10	0.546	810 ^k				16,40,26
22	Short time	0.8	4.2		.11						
23		0.8	4.2	3.3	.10	0.538	790 ^k				17,41,27
24	No pre-addn. of init.	0.8	1.8	1.9	.10	0.556	780 ^k				15,40,26
25		0.8	1.7		.09						
26		0.8	1.6		.10						
27	Lower initiator	0.8	3.8		.14						
28		0.8	3.5	3.0	.15	0.273	1400				16,40,25
29	Blank										
30	Base line	0.8	1.6	1.9	.10	0.498	820				15,38,25
31	Lower init.	0.8	1.7		.14						
32	longer time	0.8	1.6	1.5	.15	0.238	1600				16,40,26
33	Pre-reaction										
34	initiator only										

^aBD = butadiene; ^bABCPA = 4, 4'-azo-bis (4-cyanopentanoic acid); ^cTHF = tetrahydrofuran, freshly-distilled; ^dTotal volume of initiator solution in THF; ^eVolume of pure THF charged prior to BD addition; ^fOf THF solution of ABCPA; ^gOf total weight of BD, THF, and ABCPA charged; ^hWt. % of Calco in polymer; ⁱDetermined by UV; ^jblank, i.e. no initiator added; ^kBase line, i.e. arbitrarily selected standard set of conditions; ^l3 ml. of initiator solution added at room temp. just before heating was begun; ^mPurified by evaporating to dryness, dissolving in benzene, filtering benzene solution, and again evaporating to dryness.

In Runs 31, and 32, the rate of addition was kept the same as in Runs 27 and 28, but the running time (and thus the total amount of initiator) was doubled. The conversion was increased to 51% without any substantial change in molecular weight (\bar{M}_{acid} values were 1400 and 1600, respectively). Similar behavior is illustrated in Runs 23 and 24.

An interesting comparison can be made between Runs 23 and 32. Similar amounts of initiator were added (4.8 g. and 5.2 g.) but in Run 23 the addition was made in one-half hour while in Run 32 the addition was made over a 2-hour period. Hence, the actual concentration of initiator in the later run was only (about) one-fourth that used in the earlier. Under these circumstances, one would expect the molecular weight to be twice as large in the later run; \bar{M}_{acid} in Run 32 was 1600 vs. 780 in Run 23.

Based on the results of these runs, the following generalizations were made:

1. All other conditions being constant, increasing the rate of addition of the initiator decreases the molecular weight of the polymer, according to the inverse square root.
2. All other conditions being constant, increasing the amount of butadiene charged increases the molecular weight of the polymer.
3. All other conditions being constant, decreasing the amount of initiator decreases the conversion.

Production of One-Pound Lots of Azo-Initiated CTPB. — A satisfactory procedure having been established in the pilot plant for obtaining ABCPA-initiated polymer in the 300-ml. reactor, reproducibly and with the desired molecular weight, a two-gallon stirred reactor was set up for the preparation of one-pound batches of CTPB. Seven duplicate preparations were made of azo-initiated polymer at a molecular weight (\bar{M}_n) of about 4500. Reproducibility of these runs was good as indicated by the values for acid equivalents and solution viscosity shown in Table XII. Batches 8, 10, and 11 were sent to NOTS on October 19, 1965.

The acid equivalent and the dilute solution viscosity were used to monitor the pilot plant runs, because these measurements are easily carried out and are relatively insensitive to the presence of antioxidant and other contaminants. These batches of polymer closely resemble that produced by the B. F. Goodrich Chemical Company (also shown in Table XII.) The two materials have almost identical acid equivalents and dilute solution viscosities.

The procedure was then modified to produce azo-initiated CTPB of \bar{M}_n about 3000. Data for these runs are shown in Table XIII. Three of these runs (12-14) were probing experiments to establish appropriate conditions. The next four runs (15-18) were duplicates; batches 15 and 16 were shipped to NOTS on December 10, 1965.

Production of One-Pound Lots of Peroxide-Initiated CTPB. — After the production of azo-initiated polymers was completed, the preparation of one-pound lots of peroxide-initiated CTPB was begun. Table XIV shows data for several runs. The initial ones (19 through 25) were probing experiments designed to establish the conditions required to prepare one-pound batches of polymer of \bar{M}_n about 5000. Runs 26 through 29 were carried out under identical conditions. A great deal of difficulty was experienced in working up these polymers by water-washing, and they were later all found to contain precipitated solid after being stored in the refrigerator. They were then further purified by dissolving them in carbon tetrachloride and washing with aqueous isopropanol. Very nice clear products (labelled 26W, 27W, and 29W) were thereby obtained.

TABLE XII A. SCALE-UP POLYMERIZATIONS

Preparation of 1-lb. Batches of Azo-Initiated Carboxyl-Terminated Polybutadiene in 2-Gal. Reactors.										
Run No.	BD ^a (g.)	ABCPA ^b (g.)	THF ^c c' + c'' (ml.)	Time to Reaction Temp. (hr.)	Temp. (°C.)	Addn. Time ^d (hr.)	Time to Discharge (hr.)	Discharge Temp. (°C.)	Purif. Method	Polymer (g.)
1	480	e	500+100	0:13	120	1:00	0:04	15	—	4.8
2	1020	e	1000+100	1:22	120	2:00	0:03	20	—	7.9
5	1850	13	1000+100	1:26	120	2:30	0:15	20	f	365
6	1850	13	1000+100	0:06	120	2:30	0:10	10	f	365
7	1850	13	1000+100	0:06	120	3:00	0:07	30	f	445
9	1850	13	1000+100	0:10	120	3:00	0:13	20	f	401
8	1850	13	1000+100	0:08	120	3:00	0:07	20	f	462
10	2020	13	1000+100	0:06	120	3:00	0:12	20	f	423
11	1850	13	1000+100	0:10	120	3:00	0:14	20	f	403

^aBD = butadiene; ^bABCPA = 4,4'-azo-bis (4-cyanopentanoic acid); 30 ml. of initiator solution added at room temperature just before heating was begun; ^cTHF = tetrahydrofuran, freshly-distilled; ^{c'}Total volume of initiator solution in THF; ^{c''}Volume of pure THF charged prior to BD addition; ^dOf THF solution of ABCPA; ^eBlank, i.e. no initiator added; ^fPurified by evaporation to dryness, dissolving in benzene, filtering benzene solution, and again evaporating to dryness.

TABLE XII B. SCALE-UP POLYMERIZATIONS

Characterization of 1-lb. Batches of Azo-Initiated Carboxyl-Terminated Polybutadiene in 2-Gal. Reactor.												
Run No.	Shipped to NOTS ^a	Conv. (%)	Antioxidant Agent	Chgd. (%)	Found (%)	Acid Equiv. (\bar{M}_{acid})	\bar{M}_n^{obs}	\bar{M}_n^{cor}	$\langle \eta \rangle$ (1% in (C_6H_6))	\bar{M}_v	Func. (\bar{M}_n/\bar{M}_{acid})	\bar{M}_v/\bar{M}_{acid}
Goodrich ^b	—	—	Calco 2246		1.6	2340	3900	4700	.22	10,900	2.0	4.9
1		1.0										
2		0.8										
5		20	Calco 2246	2.4		2240			.23	11,500		5.1
6		20	c	1.9		2060			.23	11,500		5.6
7		24	c	0.75		2500			.22	10,900		4.4
9		22	None			2125	4300	4300	.24	12,200	2.0	5.7
8	Yes	25	c	1.5		2330			.23	11,500		4.9
10	Yes	20	Calco 2246	2.0	1.8	2200	2800	3230	.22	10,900	1.5	5.0
11	Yes	22	c		1.0	2125	3900	4690	.23	11,500	2.2	5.4

^aSamples were labelled 18974-31-8E, 18974-31-10E, and 18974-31-11E.

^bHycar CTB, Lot 13, from B.F. Goodrich Chemical Co.

^cAntioxidant supplied by NOTS.

TABLE XIII A. SCALE-UP POLYMERIZATIONS

Preparation of 1-lb. Batches of Azo-Initiated Carboxyl-Terminated Polybutadiene

Run No.	BD ^a (g.)	ABCPA ^b (g./hr.)	THF ^c c' + c'' (ml.)	Time to Reaction Temp. (hr.)	Temp. (° C.)	Addn. Time ^d (hr.)	Time to Discharge (hr.)	Discharge Temp. (° C.)	Purif. Method	Polymer (g.)
12	1850	29	1000+100	0:15	120	3:00	0:10	20	e	753
13	1850	29	1000+100	0:26	120	3:00	0:07	30	e	647
14	1850	29	1000+100	0:15	120	3:00	0:06	30	e	531
15	1396	43.5	1000+100	0:05	120	2:00	0:07	30	e	593
16	1396	43.5	1000+100	0:05	120	2:00	0:04	40	e	597
17	1396	43.5	1000+100	0:05	120	2:00	0:04	40	e	580
18	1396	43.5	1000+100	0:07	120	2:00	0:04	40	e	578

^aBD = butadiene; ^bABCPA = 4,4'-azo-bis (4-cyanopentanoic acid), 30 ml. of initiator solution added at room temperature just before heating was begun; ^cTHF = tetrahydrofuran, freshly-distilled; ^{c'}Total volume of initiator solution in THF; ^{c''}Volume of pure THF charged prior to BD addition; ^dOf the solution of ABCPA, ^ePurified by evaporating to dryness, dissolving in benzene, filtering benzene solution, and again evaporating to dryness.

TABLE XIII B. SCALE-UP RADICAL POLYMERIZATIONS

Characterization of 1-lb. Batches of Azo-Initiated Carboxyl-Terminated Polybutadiene

Run No.	Conv. (%)	Antioxidant Agent	Chgd. Found (%)	\bar{M}_{acid}	\bar{M}_n^{obs}	\bar{M}_n^{cal}	$<\eta>$ (1% in C ₆ H ₆)	\bar{M}_v	\bar{M}_n/\bar{M}_{acid}	\bar{M}_v/\bar{M}_{acid}	Shipped to NOTS
12	41	Calco 2246	1.5	1600			.21	10,300		6.4	
13	35	Calco 2246	2.2				.21	10,300			
14	38	Calco 2246	1.7				.20	9,700			
15	42	Calco 2246	1.9	1185	2800	3250	.16	7,200	2.7	6.1	Yes
16	43		0.7	1190	2700	2950	.15	6,700	2.5	5.6	Yes
17	42	None	—	1170			.16	7,200		6.2	
18	41	Calco 2246	1.9	1195	2600	3000	.16	7,200	2.5	6.1	

^aAntioxidant supplied by NOTS.

An Additional run (39) was made under the same conditions, but this was subjected only to the carbon tetrachloride-aqueous isopropanol procedure. Runs 26W and 39 were sent to NOTS on September 13, 1966.

The preparation of GAP-initiated polymer of lower molecular weight was then undertaken. In order to obtain this material, the initiator addition rate was increased fourfold over that used to prepare polymer of \bar{M}_n 5000. In the first probing runs, it was found that the formation of insoluble solid was much greater under these conditions. This, of course, was not surprising at this much increased initiator concentration. However, this larger amount of solid (about 40 grams) proved very difficult to remove. The procedure which was eventually used for these low molecular weight peroxide-initiated polymers involved dissolving them in cyclohexane, filtering, concentrating the solution, filtering again, and then evaporating completely. This process was quite satisfactory, producing polymer which remained clear on storage under refrigeration.

Runs 32-34 and 36-38 were carried out under identical conditions, except that initiator was added for an additional half hour in the second set (2½ hours vs. 2 hours) to increase the yield of polymer to the required one-pound level. Runs 37 and 38 were shipped to NOTS on July 6, 1966.

Functionality. — The difficulties in estimating functionality, the ratio of the number-average molecular weight to the equivalent weight per carboxyl group, \bar{M}_n/\bar{M}_{acid} , are described in considerable detail in another section of this report. The problem is not, of course, in the determination of \bar{M}_{acid} , but in the measurement of \bar{M}_n .

There are two feasible methods of evaluating the number-average molecular weight of these radical-initiated polymers. The number-average molecular weight of the mixture of polymer and other components can be measured and corrections made for the presence of low molecular weight contaminants. The corrected number-average molecular weights determined by this method are not very reliable, because large corrections are made on the basis of small differences.

Or the viscosity-average molecular weight can be determined from the dilute solution viscosity and converted to number-average molecular weight, provided that a reliable viscosity-molecular weight relationship is at hand and the molecular weight distribution of the sample is known.

A third possibility exists, that of washing the polymer free of contaminants and then obtaining a number-average molecular weight which need not be corrected. This approach has not been used because low molecular weight polymer would certainly be removed in this process, and the sample remaining would not truly represent the polymerization product.

In the course of the work with radical polymers, functionalities were obtained from corrected number-average molecular weights. It should be noted that \bar{M}_n^{cor} values are somewhat more reliable at lower molecular weights where \bar{M}_n^{obs} measurements are more precise and the corrections for contaminants are smaller. Although it is undesirable to put too much faith in any individual functionality value, the average of several values for the same or similar samples appears to have some validity for comparison purposes.

The functionalities thus obtained have been further examined by comparing them to values of \bar{M}_v/\bar{M}_{acid} for the same polymers.

TABLE XIV A. SCALE-UP POLYMERIZATIONS

Preparation of 1-lb. Batches of Peroxide-Initiated Carboxyl Terminated Polybutadiene.

Run No.	BD ^a (g.)	GAP ^b (g./hr.)	THF ^c c'+c" (ml.)	Time to Reaction Temp. (hr.)	Temp. (° C.)	Addn. Time ^d (hr.)	Time to Discharge (hr.)	Discharge Temp. (° C.)	Purif. Method	Polymer (g.)
19	1850	11.9	1000+100	0:39	120	3:00	0:04	60	e	—
20	1850	11.9	1000+100	0:04	120	3:00	0:09	35	f	—
21	1850	11.9	1000+100	0:11	120	3:00	0:09	40	g	—
22	1935	11.9	1000+100	0:15	120	3:00	0:12	30	h	327
23	1850	0	1000+100	0:05	120	3:00	0:04	35	—	<49
24	1850	16.6	1000+100	0:06	120	3:00	0:17	40	i	380
25	1850	16.6	1000+100	0:15	120	3:00	0:06	20	j	—
26	1850	16.0	1000+100	0:15	120	4:00	0:06	30	i (26W,h)	607
27	1850	16.0	1000+100	0:15	120	4:00	0:05	30	i (27W,h)	528
28	1850	16.0	1000+100	0:17	120	4:00	0:05	85	i	591
29	1850	16.0	1000+100	1:05	120	4:00	0:03	90	i (29W,h)	544
39	1814	16.0	1000+100	0:05	120	4:00	—	—	h	517
30	1814	64.0	1000+100	0:15	120	1:00	0:02	80	k	379
31	1814	64.0	1000+100	0:11	100	1:00	0:03	90	l	164
32	1362	36.0	1000+100	0:06	120	2:00	0:05	—	i	270
33	1362	36.0	1000+100	0:11	120	2:00	0:06	100	i	206
34	1362	36.0	1000+100	0:12	120	2:00	—	—	l	347
35	1362	—	—	—	—	—	—	—	—	—
36	1362	36.0	1000+100	0:09	120	2:30	—	—	l	402
37	1362	36.0	1000+100	0:09	120	2:30	—	—	l	465
38	1362	36.0	1000+100	0:10	120	2:30	—	—	l	517

^aBD = butadiene; ^bGAP = glutaric acid peroxide, 30 ml. of initiator solution added at room temperature just before heating was begun, ^cTHF = tetrahydrofuran, freshly-distilled; ^{c'}Total volume of initiator solution in THF, ^{c''}Volume of pure THF charged prior to BD addition; ^dOf the solution of GAP, ^ePurified by evaporating to dryness, dissolving in 3:1 cyclohexane-benzene solution and evaporating after filtering; ^fSame as (e) plus water washing; ^gSolution in CHCl₃, filtration and evaporation of solvent followed by e; ^hCCl₄ solution, C₃H₇OH extraction and evaporation after filtering; ⁱBenzene solution washed with water, ^jMechanical problems terminated run; ^kPurified by evaporating to dryness, dissolving in benzene, water-washing benzene solution, evaporating to dryness, dissolving in cyclohexane, filtering, and evaporating to dryness, ^lSolution in cyclohexane, filtration, partial removal of solvent, filtration, complete removal of solvent.

TABLE XIV B. SCALE-UP POLYMERIZATIONS

Characterization of 1-lb. Batches of Peroxide-Initiated Carboxyl-Terminated Polybutadiene

Run No.	Conv. (%)	Antioxidant Agent	Chgd. Found (%)	\bar{M}_{acid}	\bar{M}_n^{cor}	$\langle \eta \rangle$ (1% in C_6H_6)	\bar{M}_v	\bar{M}_w/\bar{M}_{acid}	\bar{M}_v/\bar{M}_{acid}	Shipped to NOTS
19	—	Calco 2246		2890		.26	13,500		4.7	
20	—	Calco 2246		2190		.27	14,200		6.5	
21	—	Calco 2246				.27	14,200			
22	17	Calco 2246	1.8			.28	14,900			
23	<3	—								
24	20	Calco 2246	2.4	2440		.25	12,800		5.2	
25	—	Calco 2246		2380		.25	12,800		5.4	
26	33	Calco 2246	1.5	2420		.26	13,500		5.6	
26W				1.7	2790	5500	.26	13,500	4.8	Yes
27	29	*	0.9			.28	14,900		6.2	
27W				0.3	3170		.27	14,200	4.5	
28	32	Calco 2246	1.5	2260		.26	13,500		6.0	
29	29	None	—	2190		.24	12,200		5.6	
29W				2650		.23	11,500		4.3	
39		Calco 2246	1.1	2760		.25	12,800		4.6	Yes
30	20	Calco 2246	2.7	1295		.19	9,000		6.9	
31	9	Calco 2246	6.1			.16	7,200			
32	20	Calco 2246	3.6			.17	7,800			
33	15	Calco 2246	4.9			.15	6,700			
34	28	Calco 2246	2.6	1285		.18	8,400		6.5	
35	—	—								
36	30	Calco 2246	2.5			.16	7,200			
37	34	Calco 2246	2.1	2.0	1275	3400	.17	7,800	2.7	Yes
38	38	*	1.0	0.3	1150		.17	7,800	6.1	Yes

*Antioxidant supplied by NOTS.

The ratio of viscosity-average molecular weight to acid equivalent is equal to the functionality times a heterogeneity factor as shown below.

$$\frac{\bar{M}_v}{\bar{M}_{acid}} = \underbrace{\frac{\bar{M}_n}{\bar{M}_{acid}}}_{\text{functionality}} \times \underbrace{\frac{\bar{M}_v}{\bar{M}_n}}_{\text{heterogeneity factor}}$$

As would be expected, there is a correlation between functionality and \bar{M}_v/\bar{M}_{acid} for CTPB samples polymerized in similar fashion and subjected to similar work-up procedures. If more branching takes place in one case than another, the functionality, of course, increases (provided the proportion of non-functional ends is unchanged). The heterogeneity factor also becomes greater, since \bar{M}_v increases with branching faster than does \bar{M}_n . And, of course, \bar{M}_v/\bar{M}_{acid} reflects both of these increases.

Table XV shows data for several azo- and peroxide-initiated polymers prepared under varying conditions and having varying molecular weights. The values for \bar{M}_n^{cor} were calculated from the number-average molecular weights as measured by vapor phase osmometry; the antioxidant contents were in general determined by ultraviolet spectroscopy.

Viscosity-average molecular weights were computed from the dilute solution viscosities by means of the relationship of Stacy and Gregg.⁹

$$[\eta] = 1.56 \times 10^{-4} \bar{M}_v^{0.78}$$

It would be interesting to calculate \bar{M}_v values from the equation recently published by workers at Aerojet⁸. However, it might be noted that in the present work, \bar{M}_v values have not been used to calculate \bar{M}_n , but that \bar{M}_v has been considered only in relation to \bar{M}_{acid} . Errors in the absolute values of \bar{M}_v are not so important then, provided that relative values have some validity.

TABLE XV A. FUNCTIONALITY AND \bar{M}_v/\bar{M}_{acid} DATA FOR VARIOUS AZO-INITIATED POLYMERS.

Run No.	Conv. (%)	\bar{M}_{acid}	\bar{M}_n^{obs}	\bar{M}_n^{cor}	$\bar{M}_n^{cor}/\bar{M}_{acid}$	$\langle \eta \rangle$ (1% in C_6H_6)	\bar{M}_v	\bar{M}_v/\bar{M}_{acid}
Low molecular weight (Table VIII); laboratory; incremental addition; 117°C.; 0-5-2.0 hr.								
A47	49	810	1910	2100	2.6	.12	5000	6.2
A51	26	980	1670	2250	2.3	.14	6100	6.2
A52	33	1030	2030	2750	2.7	.15	6700	6.5
B2	21	1370	1880	3050	2.2	.20	9700	7.1
B4	37	1080	2090	2500	2.3	.16	7200	6.7
Low molecular weight (Tables X and XI); pilot plant background studies in 300-ml. reactor; continuous addition; 120°C.; 1 hr.								
8	50	820	1650	1725	2.1	.11	4500	5.5
9	47	840	1520	1625	1.9	.10	4000	4.7
10	42	850	1650	1705	2.0	.09	3500	4.1
11	52	925	1540	1620	1.8	.11	4500	4.9
12	47	960	2020	2185	2.3	.09	3500	3.8

TABLE XV A. FUNCTIONALITY AND \bar{M}_v/\bar{M}_{acid} DATA FOR VARIOUS AZO-INITIATED POLYMERS -- CONTINUED

Run No.	Conv. (%)	\bar{M}_{acid}	\bar{M}_n^{obs}	\bar{M}_n^{cor}	$\bar{M}_n^{cor}/\bar{M}_{acid}$	$\langle\eta\rangle$ (1% in C_6H_6)	\bar{M}_v	\bar{M}_v/\bar{M}_{acid}
Low molecular weight (Table XII); pilot plant 2-gal. reactor; continuous addition; 120°C.; 2 hr.								
15	42	1185	2800	3250	2.7	.16	7200	6.1
16	43	1190	2700	2950	2.5	.15	6700	5.6
17	42	1170				.16	7200	6.2
18	41	1195	2600	3000	2.5	.16	7200	6.1
High molecular weight (Table XII), pilot plant 2-gal. reactor; continuous addition; 120°C.; 3 hr.								
5	20	2240				.23	11500	5.1
6	20	2060				.23	11500	5.6
7	24	2500				.22	11000	4.4
9	22	2125	4300	4300	2.0	.24	12000	5.7
8	25	2330				.23	11500	4.9
10	21	2200	2800	3230	1.5	.22	11000	5.0
11	22	2125	3900	4690	2.2	.23	11500	5.4

TABLE XV B. FUNCTIONALITY AND \bar{M}_v/\bar{M}_{acid} DATA FOR VARIOUS PEROXIDE-INITIATED POLYMERS

Run No.	Conv. (%)	\bar{M}_{acid}	\bar{M}_n^{obs}	\bar{M}_n^{cor}	$\bar{M}_n^{cor}/\bar{M}_{acid}$	$\langle\eta\rangle$ (1% in C_6H_6)	\bar{M}_v	\bar{M}_v/\bar{M}_{acid}
Low molecular weight (Table V-Appendix); laboratory, incremental addition; 95°C.; 3 hr.								
27	32	1240	3160	3800	3.1	.20	9700	7.8
35	28	535	1520	1725	3.2	.10	4000	7.5
Low molecular weight (Table XIV); pilot plant 2-gal. reactor; continuous addition; 120°C.; 2.5 hr.								
54	28	1285				.18	8400	5.5
37	38	1150				.17	7800	6.7
38	34	1275	2900	3400	2.7	.17	7800	6.1
High molecular weight (Table XIV); pilot plant 2-gal. reactor; continuous addition; 120°C.; 4 hr.								
26W	33	2790		5500	2.0	.26	13500	4.8
27W	29	3170				.27	14200	4.5
29W	29	2650				.23	11500	4.3
39	29	2760				.25	12800	4.6

Although there is considerable scatter in the functionality and \bar{M}_v/\bar{M}_{acid} data shown in Table XV within any one set, the averages behave in a fairly consistent manner. Thus, when the functionality is close to 2.0, \bar{M}_v/\bar{M}_{acid} is close to 5. As the functionality increases to 2.5 and then to 4.0, \bar{M}_v/\bar{M}_{acid} increases toward a value of about 8. Figure 8 illustrates this relationship graphically.

It is interesting to consider what factors affect branching and hence functionality in these radical-initiated polymers. Two trends have been noted. The polymers produced in the pilot plant have had lower functionalities than those prepared in the laboratory. And the one-pound

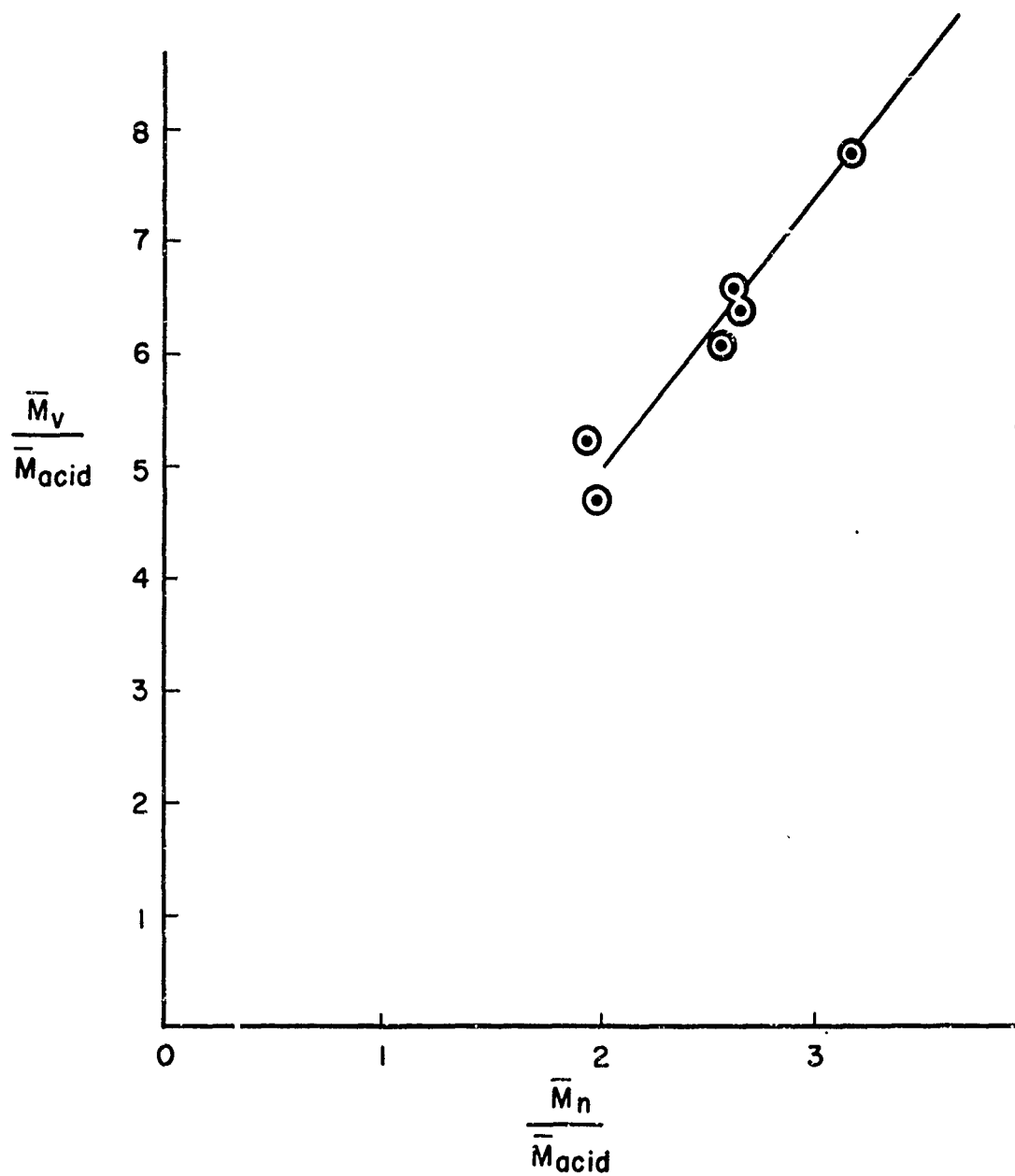


FIGURE 8. Relationship of \bar{M}_v/\bar{M}_{acid} to \bar{M}_n/\bar{M}_{acid} (Functionality) in Radical-Initiated CTPB.

batches of "low" molecular weight CTPB, whether azo- or peroxide-initiated, have shown higher functionalities than the "high" molecular weight lots.

The critical difference between the laboratory and pilot plant procedures seems to be in the manner of initiator addition. In the laboratory, initiator was added incrementally (or even in a single charge), whereas in the pilot plant it was added continuously. Functionalities as high as 3.0 have been found for polymers prepared by incremental addition, from both the azo and the peroxide initiators. With continuous addition, functionalities close to 2.0 appear to have been obtained for both polymers.

As for the differences in the functionality of the "high" and "low" molecular weight polymers, this is not thought to be related to the molecular weight *per se*, but a consequence of differing experimental conditions. And low molecular weight CTPB of functionality close to 2.0 has been obtained in a different experimental set-up (see Table X). Functionality would not be expected to increase with decreasing molecular weight. If anything, one would predict that functionality would increase with increasing molecular weight because of the greater probability of a long molecule, with its larger number of double bonds, undergoing crosslinking than a short molecule.

It is possible that both the difference between incremental and continuous addition of initiator and the difference between "high" and "low" molecular weight one-pound lots of polymer can be traced to initiator concentration. With incremental addition, the concentration of initiator is, of course, very high immediately after each addition. And, a comparison of conditions used to prepare the one-pound lots shows that the initiator concentration is considerably greater for the "low" molecular weight product than for the "high" molecular weight material.

It is not understood why a change in initiator concentration should affect branching. And it is possible that this apparent relationship is an artifact and that some other influence is actually operative. Among the other factors which have been considered are polymer concentration and conversion.

Normally, polymer concentration would be expected to have an important effect on branching. As the concentration of polymer increases, more branching should take place, since collisions of growing radicals with existing chains would occur more frequently. In most polymerization systems, the polymer concentration is directly related to the conversion. And both, of course, increase during the course of the reaction.

It is now realized that in the present system, however, in which solvent is added throughout the polymerization, the polymer concentration actually changes very little during the reaction. Even in dissimilar runs (i.e., azo- and peroxide-initiated of "high" and "low" molecular weight), the polymer concentrations are not found to be very different. This is perhaps not too surprising in view of the fact that the same reactor was used to make the same amount of polymer in about the same amount of time. The polymer content per volume of solution was also nearly the same. Typical experimental conditions are seen in Table XVI.

Thus, conversion appears to have very little effect on the polymer produced (at least up to conversions of about 50%). In a pair of experiments in which one run was continued for twice as long as the other (Runs 28 and 32 in Table XI), the conversion was increased from 24% to 51%. Values for \bar{M}_{acid} were 1400 and 1600, respectively, and for the inherent viscosity 0.15 in both cases.

For a time, it was thought that more branching occurs with glutaric acid peroxide as initiator than with 4,4'-azo-bis(4-cyanopentanoic acid). And, indeed, this would not be unreasonable

since the primary radicals generated by the peroxide would be expected to be more reactive than the tertiary radicals formed from the azo compound. (Note that this hypothesis demands that the attack of radicals on polymer be predominantly by the initiator radicals themselves.) It was also thought to be suggestive of branching that there is an odor of butyric acid in the peroxide-initiated polymer before its purification.

However, in the pilot plant when similar conditions were used to prepare azo- and peroxide-initiated CTPB, similar products were obtained as shown in Table XV. It is true that the work-up procedures were not identical and that the water-washed high molecular weight peroxide-initiated polymers, in particular, may not be completely comparable. Nevertheless, at the present time, no basis exists for concluding that there is more branching with the peroxide initiator than with the azo initiator.

TABLE XVI. TYPICAL CTPB PREPARATIONS YIELDING 400-600 GRAMS OF POLYMER.

"High" Molecular Weight Azo-Initiated CTPB	"High" Molecular Weight Peroxide-Initiated CTPB
1850 g. Butadiene 39 g. ABCPA (13 g./hr.)	1850 g. Butadiene 64 g. GAP (16 g./hr.)
1100 cc. Tetrahydrofuran	1100 cc. Tetrahydrofuran
120°C.	120°C.
3 hr.	4 hr.
22% Conversion	30% Conversion
"Low" Molecular Weight Azo-Initiated CTPB	"Low" Molecular Weight Peroxide-Initiated CTPB
1400 g. Butadiene 87 g. ABCPA (43.5 g./hr.)	1350 g. Butadiene 90 g. GAP (36 g./hr.)
1100 cc. Tetrahydrofuran	1100 cc. Tetrahydrofuran
120°C.	120°C.
2 hr.	2.5 hr.
42% Conversion	36% Conversion

Bulk Viscosity of Carboxyl-Terminated Polybutadiene. — The bulk viscosity of samples of the higher molecular weight azo- and peroxide-initiated polymers was measured and also that of the four commercial polymers. The bulk viscosity of the azo-initiated polymer is higher than that of CTPB obtained by the other methods (at comparable molecular weights). This effect has been attributed by workers at the Thiokol Chemical Corporation⁴ to interactions involving the nitrile groups of neighboring chains. Table XVII shows data obtained at 3M.

TABLE XVII. BULK VISCOSITY OF VARIOUS SAMPLES OF CTPB

	Brookfield Viscosity 3RPM, $76 \pm 2^\circ\text{F}$. (poises)	Equiv. Wt. per Carboxyl Group (M_{acid})	$\langle\eta\rangle$ (1% in benzene)
Radical systems			
Azo-initiated			
3M	442	2200	0.22
Goodrich ^a	554	2340	0.22
Peroxide-initiated			
Thiokol ^b	264	1900	0.22
Anionic systems			
Phillips ^c	384	2690	0.21
General Tire ^d	228	2760	0.19

^aHycar CTB, Lot 13, B. F. Goodrich Chemical Company.

^bHC 434, Lot 19, Thiokol Chemical Corporation.

^cButarez CTL-2, Lot 303, Phillips Petroleum Company.

^dTelagen Liquid Rubber, 596-720, General Tire and Rubber Company

Some bulk viscosity data were also reported in a British patent issued to the Thiokol Chemical Corporation.² These are shown in Table XVIII.

TABLE XVIII. BULK VISCOSITY DATA TAKEN FROM THIOKOL PUBLICATION

Molecular Weight	Viscosity (Poises)	
	Azo (ABCPA)	Peroxide (GAP)
3000	300	120
4000	750	220
5000	1500	380

Their values for the bulk viscosity of ABCPA-initiated polymer appear high, although their data for GAP-initiated material correspond closely with that obtained here.

A high bulk viscosity is, of course, undesirable for propellant binder applications, and the use of a lower molecular weight CTPB might be required in the case of the azo-initiated polymer. Normally a material with shorter primary chains would be expected to produce a cured polymer with poorer physical properties. However, since the carboxyl groups in the azo-initiated polymer appear to undergo chain extension reactions more rapidly and to a greater extent than do the carboxyls of the other varieties of CTPB (see section on chain extension), this may not necessarily be the case.

Chain Extension Studies

A study of the reaction of the various types of CTPB with a pure difunctional chain extender was undertaken. A sample of purified HX-742 (N,N'-bis(ethylene)isophthalamide) was obtained from the 3M Chemical Division. This material is reported to have a purity of 99.0% (38.5% imine ring structure). Dilute solution viscosity data were used to measure the extent to which chain extension occurs. It was hoped thus to gain some insight into the functionality distribution of the different polymers.

The situation is complicated by the fact that the carboxyl groups in the various types of CTPB do not necessarily have the same reactivity. Furthermore, the aziridine group in the chain extender can isomerize to the oxazoline structure; it can also undergo homopolymerization, leading to crosslinking where otherwise only chain extension would be possible. Thus, it is difficult to use chain extension data directly to prove that a particular type of CTPB has the highest content of difunctional material. However, it should be possible to determine which sample within a particular type of CTPB is the most difunctional.

Several experiments were carried out to gain experience with the chain extension reaction. Thus, the reaction was run with and without heating, and with and without zirconium acetylacetonate catalyst.

As expected, the reaction was very slow when neither heat nor catalyst was used. (Table XIX). The rate was increased somewhat when catalyst was added, but the mixture was not heated. Heat alone was found to cause some increase in viscosity, but the combination of heat and catalyst was, of course, the most effective.

The Goodrich polymer was found to undergo the greatest increase in viscosity upon addition of chain extender. It is, of course, well known that this material cures **more rapidly** than do the other types of CTPB. However, the Goodrich material also reacts to a **greater extent**. Thus, this polymer underwent a nine-fold increase in molecular weight upon treatment with 1.05 equivalents of chain extender, while the others increased only about six-fold. The greater reactivity of the carboxyl groups in the Goodrich polymer may be due to the electron-withdrawing character of the nitrile group.

In none of these chain extension experiments did immediate crosslinking occur. All of the samples, both heated and unheated, have proved completely soluble. However, on longer standing crosslinking has taken place, particularly in very concentrated solutions or in solvent-stripped samples. Goodrich samples containing from 0.90 to 1.30 equivalents of chain extender were found to have undergone chain extension without gelation upon being heated at 60°C. for 50 hours. The inherent viscosities of these samples are shown in Table XIX. The samples containing 1.00, 1.05, and 1.10 equiv. were found to have gelled after having been stripped of solvent and standing for one week; the other samples had increased further in viscosity. A similar set of General Tire samples were found to have gelled completely after three weeks.

TABLE XIX. CHAIN EXTENSION STUDIES OF COMMERCIAL POLYMERS
WITH N,N'-BIS (ETHYLENE) ISOPHTHALAMIDE (PURIFIED HX 742)

a. UNCATALYZED REACTION AT ROOM TEMPERATURE

	Equiv. Wt. of Polymer	Amounts Used		Inherent Viscosity, $\langle \eta \rangle$, 1% in Benzene Untreated Polymer	Polymer plus Chain Extender	
		Polymer (g.)	Purified HX 742 (g.)		36 hr.	18 da.
1) Thiokol ^a	1900	5.0152	.285	0.22	0.21	0.23
2) Goodrich ^b	2340	5.0164	.232	0.22	0.23	0.26
3) Phillips ^c	2690	5.1580	.207	0.22	0.23	0.24
4) General Tire ^d	2760	5.0041	.196	0.19	0.19	0.21

Carried out in benzene solution containing 18 wt.% of polymer; chain extender was added in the ratio of 1.00 equivalents per polymer acid equivalent.

^aHycar CTB, Lot 13, B. F. Goodrich Chemical Company

^bHC 434, Lot 19, Thiokol Chemical Corporation

^cButarez CTL-2, Lot 303, Phillips Petroleum Company

^dTelagen Liquid Rubber, 595-720, General Tire and Rubber Company.

b. EFFECT OF HEAT OR CATALYST ALONE ON THIOKOL POLYMER

	Inherent Viscosity, $\langle \eta \rangle$, 1% in Benzene	
	16 hr.	14 da.
1) Polymer plus chain extender at room temperature	0.19	0.23
2) Polymer plus chain extender, heated 16 hr. at 70°C.	0.26	0.27
3) Polymer plus chain extender plus catalyst at room temperature	0.22	0.24

Master batch was made up of 15.0168 g. (.007904 equiv.) of Thiokol polymer (\bar{M}_{acid} , 1900), 0.8530 g. (.007898 equiv.) of chain extender, 26.4 g. benzene. Mixture was 35.6 wt. % polymer. Sample 3 was made up by adding .02 g. of zirconium acetylacetonate to 13.8 g. of master batch; catalyst is 0.4 wt. % of polymer.

c. EFFECT OF HEAT AND CATALYST ON THICKOL POLYMER CONTAINING VARYING AMOUNTS OF CHAIN EXTENDER

Polymer (g.)	Purified HX 742 (g.)	Equiv. of Chain Extender per Equiv. of Polymer	Inherent Viscosity, $\langle \eta \rangle$, in 1% Benzene Unheated Controls	Samples after 50 hr. at 62°C.
2.8427	0.1454	0.90	0.31	0.49
2.8507	0.1539	0.95	0.32	0.51
2.8561	0.1623	1.00	0.32	0.61
2.8549	0.1785	1.10	0.34	0.67

Master batch was made up from 20.0192 g. of HC 484, Lot 13, Thiokol Chemical Corporation (\bar{M}_{acid} , 1900), 0.2025 g. (1.0 wt. % of polymer) of zirconium acetylacetonate and 21.975 g. of benzene, giving a mixture 47.4 wt. % in polymer. Portions were weighed out containing amounts of polymer as shown above.

d. COMPARISON OF COMMERCIAL POLYMERS UPON TREATMENT WITH HEAT, CATALYST, AND 1.05 EQUIVALENTS OF CHAIN EXTENDER

	\bar{M}_{acid}	Polymer (g.)	ZrAA (g.)	Purified HX 742 (g.)	Benzene (g.)	Untreated Polymer $\langle \eta \rangle$ (1% in C_6H_6)	Polymer Plus Chain Extender After 44 hr. at 60°C. $\langle \eta \rangle$ (0.1% in C_6H_6)
Thiokol	1900	12.008	.0841	0.7175	19.631	0.22	0.86
Goodrich	2340	12.419	.0869	0.6025	20.248	0.22	1.20
Phillips	2690	12.416	.0869	0.5240	20.243	0.21	0.94
General Tire	2760	12.369	.0866	0.5088	20.173	0.19	0.97

(Samples were 37 wt. % polymer. Catalyst was 0.7 wt. % of polymer.)

e. EFFECT OF HEAT AND CATALYST ON GOODRICH POLYMER CONTAINING VARYING AMOUNTS OF CHAIN EXTENDER

Polymer (g.)	Purified HX 742 (g.)	Equiv. of Chain Extender per Equiv. of Polymer	Inherent Viscosity, $\langle \eta \rangle$, in Benzene after 24 Hrs. at 60°C. and 72 Hrs. at Room Temp. Quenched 7 Days at room temp. after solvent removed
3.1892	0.1325	0.90	0.74
3.1900	0.1399	0.95	1.04
3.1854	0.1470	1.00	1.05
3.1790	0.1541	1.05	1.10
3.1792	0.1614	1.10	0.97
3.1803	0.1761	1.20	0.75
3.1827	0.1906	1.30	0.63
			0.90
			1.52
			gel
			gel
			gel
			1.16
			0.90

Master batch was made up from 24.9551 g. of Hycar CTB, Lot 13, B. F. Goodrich Chemical Company (\bar{M}_{acid} , 2340), 0.1747 g. (0.7 wt. % of polymer) zirconium acetylacetonate, and 21.975 g. of benzene, giving a mixture 53.0 wt. % in polymer. Portions were weighed out containing amounts of polymer as shown above.

B. ANIONIC POLYMERIZATION

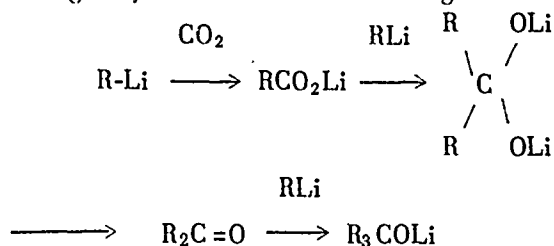
General Considerations

The anionic polymerization of butadiene may be carried out using alkali metals, their complexes as with naphthalene, or their dimetallo derivatives of hydrocarbons as initiators. Most of the literature concerning the preparation of CTPB by anionic methods is contained in patents issued to the Phillips Petroleum Company. These patents most commonly describe the use of dimetallo derivatives of hydrocarbons as initiators in a hydrocarbon solvent system. It has been stated¹⁰ that initiators based on lithium as the alkali metal are preferred, and almost all of the literature concerning anionic CTPB describes only the use of lithium for initiator preparation.

Anionic polymerization is potentially a more versatile technique for preparing CTPB than polymerizations using free radical initiators. Under the proper conditions, anionic polymerization is capable of yielding polymer having a very narrow molecular weight distribution. This is desirable for CTPB in order to achieve adequate strength in the cured polymer and still have a bulk viscosity low enough to permit easy processing. Also, the microstructure of the polymer can be varied considerably by varying the solvent system used for the polymerization. Thus, polar solvents tend to increase the amount of 1,2-addition while non-polar solvents give predominantly 1,4-addition. Anionic preparations of CTPB would be expected to result in less chain branching than radical polymerizations, thus permitting polymerizations to be carried out to higher conversions.

As in all anionic polymerizations, great care must be taken to exclude water and oxygen during the preparation of CTPB by anionic methods. All equipment must be thoroughly dried, all reagents carefully purified and all operations must be carried out in an inert atmosphere.

After completion of the anionic polymerization of butadiene, the polymer is given its carboxyl termination by reaction with carbon dioxide. This step in the preparation of anionic CTPB also presents difficulties since chain extension reactions (of the type reported by Wyman, Allen and Altares for polystyrene¹¹) can occur, yielding dipolybutadiene ketone and tripolybutadiene carbinol; these would greatly broaden the molecular weight distribution.



Initiator System

Lithium-Naphthalene in Tetrahydrofuran. — Since the preparation of carboxyl-terminated polybutadiene via lithium-naphthalene initiator in tetrahydrofuran solution has been well described by Hayashi and Marvel¹², this method was the first to be examined. Several runs were carried out using this system, all of which resulted in polymers having a rather low carboxyl content. While the results are somewhat inconclusive, since techniques of monomer purification, carbonation, etc., were also being developed during this investigation, it was found that this system has the following disadvantages.

1. The polymer produced is predominantly (>90%) of 1,2-structure. It is expected that this would probably lead to rather poor mechanical properties in a vulcanizate.
2. The polymerization temperature must be kept very low since the amount of carboxyl termination decreases at higher temperatures. This effect is shown in Table XX in which the polymerizations were carried out under the same conditions except for temperature.

The reason for the decrease in carboxyl content at higher temperatures is probably due to reaction of alkylolithium compounds with tetrahydrofuran. Morton, Rembaum and Hall¹³ have reported that reactions of this type occur at temperatures of -35° or higher. This necessity of working at low temperatures results in extremely viscous reaction mixtures which are very difficult to stir and carbonate effectively.

TABLE XX
ANIONIC POLYMERIZATION IN TETRAHYDROFURAN

Run No.	Temp. ($^{\circ}$ C.)	Eq. Wt. per CO_2H Group
1	0	22,000
2	-20	6,950
3	-40	3,950

3. Tetrahydrofuran is very difficult to purify. The most effective purification technique involves preparing a solution of "living polymer" in tetrahydrofuran and distilling the solvent from this solution immediately prior to use. This procedure is laborious and time-consuming, particularly for larger volumes of solvent.

Lithium-Stilbene in Toluene. — The use of dilithiodiphenylethane (lithium stilbene) as an initiator for the preparation of CTPB has been described in a number of patents issued to the Phillips Petroleum Company (e.g. reference 14).

This initiator is prepared by reacting lithium and stilbene in tetrahydrofuran. The initiator solution is then added to a hydrocarbon solvent (toluene or cyclohexane) and part of the tetrahydrofuran removed by distillation. Polymerization in this system results in much less 1,2-addition than is obtained in tetrahydrofuran alone.

A brief investigation of this initiator system showed that dilithiodiphenylethane has only a limited solubility in hydrocarbon solvents. This resulted in polymerizations in which it was difficult to control molecular weights and achieve reproducibility. If the amount of tetrahydrofuran left in the polymerization was sufficient to solubilize the initiator, better control could

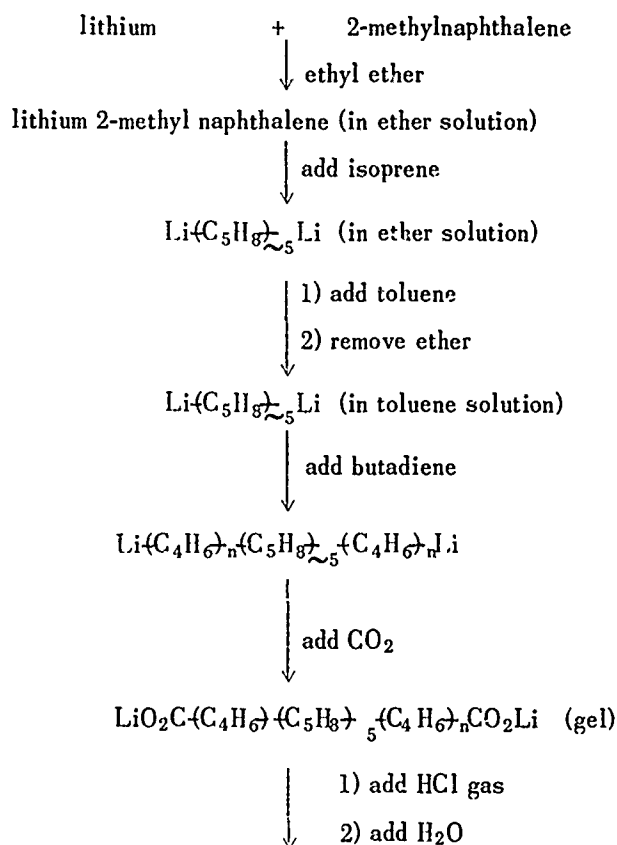
be achieved; however, the reaction was then subject to the same disadvantages noted for the lithium-naphthalene-tetrahydrofuran system.

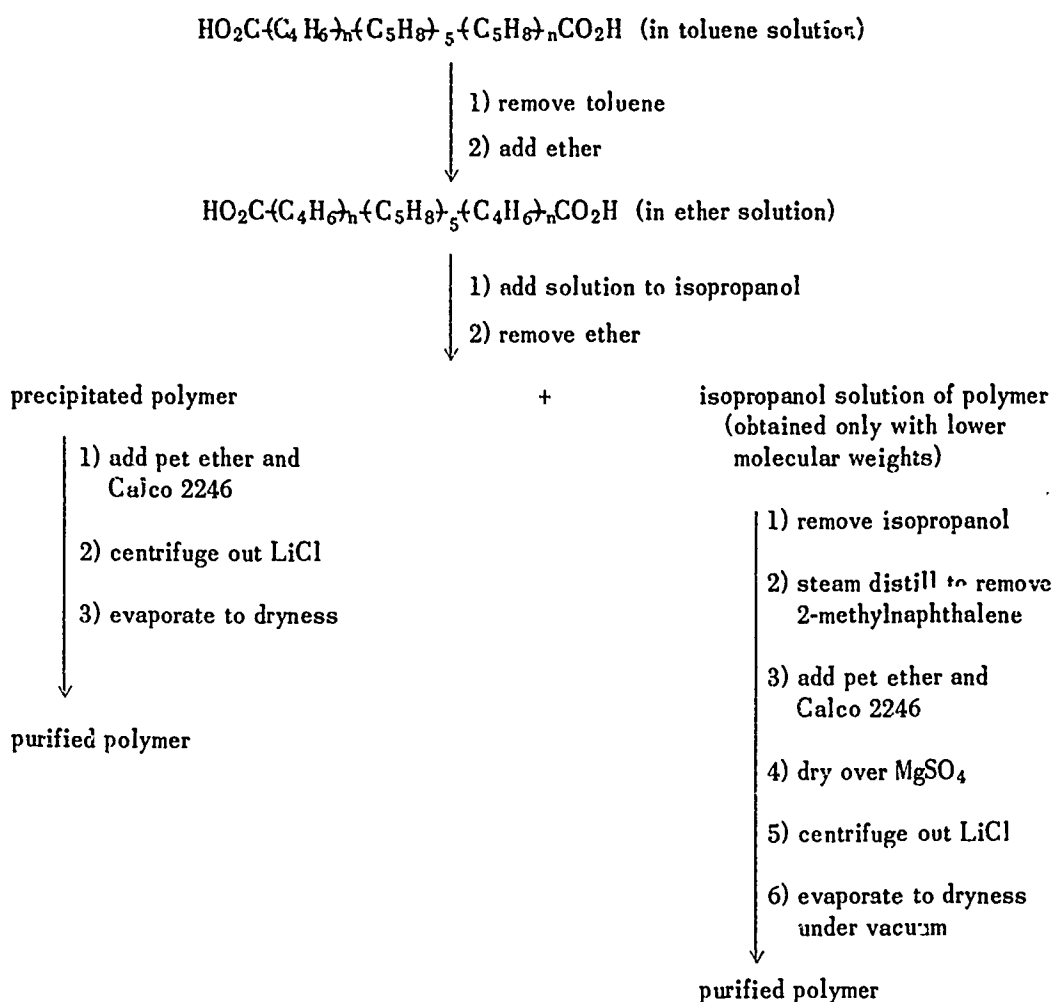
One run was tried in which dilithiotetraphenylethane in toluene was used to initiate the polymerization. While this initiator appeared to be more soluble than dilithiodiphenylethane, its solubility was still not complete.

On the basis of the above results, it is felt that a prime requirement for the preparation of satisfactory anionic CTPB is an initiating system which is soluble in hydrocarbon solvents.

Dilithiopolyisoprene. — It has been reported¹⁵ by workers at Phillips Petroleum Company that low molecular weight lithium-terminated polymers of dienes such as isoprene or 2,3-dimethylbutadiene can be prepared in ethyl ether solution. These polymers are soluble in hydrocarbon solvents and will initiate the polymerization of butadiene. Due to the increased solubility of these initiators, it was felt that these systems offered the most promise as a means of preparing satisfactory CTPB by anionic methods. Therefore, most of our effort in the area of anionic polymerization has involved the use of dilithiopolyisoprene as the initiator. A number of polymerization parameters have been investigated using this initiator system. The results of these investigations are discussed in the following sections.

Polymerization Procedure. — A schematic diagram of the procedures used for most of the runs involving the dilithiopolyisoprene initiator system is shown below:





Preparation of Initiator. — The initiator solution most commonly used is prepared by first reacting excess lithium dispersion with 2-methylnaphthalene in ethyl ether. 2-Methylnaphthalene is used rather than naphthalene itself because of its much greater reactivity, thus permitting the use of ethyl ether rather than tetrahydrofuran, which simplifies removal of ether from the polymerization. Isoprene is then added to this solution using an amount calculated to give an isoprene chain of 5 to 10 units in length. This mixture was found to be very effective for purifying butadiene (see below). For polymerization, the ether solution is mixed with the polymerization solvent and most of the ether removed by distillation at reduced pressure to give a solution of dilithiopolyisoprene in a hydrocarbon solvent. Later results indicated it was also desirable to filter this solution (see Section on Molecular Weight Distribution).

In order to check the quality of the dilithiopolyisoprene initiator, a run was made in which the initiator solution itself was carbonated. Analysis of the resulting low molecular weight carboxyl-terminated polyisoprene showed it was of the expected chain length and had a functionality close to two. This result indicated that this type of initiator and the procedures used for its preparation were satisfactory.

Age of Initiator Solution. — It was found that the age of the solution of dilithiopolyisoprene used to initiate CTPB had a pronounced effect upon the carboxyl content of the polymers obtained. This effect is shown in Table XXI for three different initiator solutions. All of the polymerizations using a particular initiator solution were carried out in the same way and molecular weights of the polymers within each set were of the same order of magnitude as indicated by viscosity measurements. In subsequent runs, this effect was minimized by preparing the initiator solution immediately prior to polymerization.

TABLE XXI. EFFECT OF AGE OF INITIATOR SOLUTION ON
FUNCTIONALITY OF ANIONIC CTPB.

Run No.	Initiator Solution	Age of Initiator Sol'n. (days)	$\langle \eta \rangle$ of Polymer (1% in CH_2)	Acid Eq. Wt.
18557-11	A	1	.11	1230
-13	A	7	.14	3050
-14	A	15	.14	3850
18557-17	B	5	.18	3810
-18	B	12	.15	4945
18557-24	C	1	.30	3900
-25	C	2	.31	5650

Butadiene Purification. — A number of methods of obtaining butadiene of sufficient purity for anionic polymerization were investigated. The first method studied has been described in the literature¹² and involves passing the gaseous monomer through a solution of sodium ethylene glycolate in ethylene glycol, followed by passage through columns of Drierite and silica gel. This procedure was found to be inadequate as judged by the fact that all polymerizations using monomer purified in this manner gave products of very low carboxyl content.

It was found that better results could be obtained by refluxing butadiene over freshly-cut sodium for several hours. However, this technique is time consuming and proved to be non-reproducible.

The best method found for purification of butadiene consists of "titrating" the liquid monomer with a "living polymer" solution until the characteristic color of the "living polymer" persists, and then distilling unreacted butadiene from this mixture. The initiator solution prepared as described above from ether, lithium, 2-methylnaphthalene and isoprene was found to work very well for this purpose. This technique was also used to check the purity of butadiene purified by the other methods described above. Addition of a small amount of initiator solution to the "purified" butadiene resulted in immediate decoloration of the initiator, thus indicating the monomer still contained impurities.

Polymerization Conditions. — The polymerization reaction has been carried out by rapidly distilling purified butadiene into a solution of the dilithiopolyisoprene initiator, using a Dry Ice cooled condenser to maintain the butadiene in the reaction zone. The reaction mixture is then stirred vigorously until polymerization appears to be complete (1-2 hours) as judged by the mixture achieving a constant viscosity.

Two temperatures, 50° and 25°, have been used. No significant differences have been noted in polymers prepared at the two temperatures. At 50°, the viscosity of the polymerization

solution is lower which facilitates stirring. However, at 25°, the solubility of butadiene in the reaction solvent is much greater than at 50°. It is probably desirable to have as much of the butadiene as possible in solution throughout the polymerization in order to achieve a more uniform chain length, and for this reason, the lower temperature is preferred. At still lower temperatures, reaction times become long and viscosities very high causing difficulties in stirring and carbonating the polymer.

The ratio of butadiene to solvent is a rather critical factor in the preparation of anionic CTPB. If the weight of butadiene polymerized exceeds about 10-12% of the volume of solvent, the viscosity of the polymerization mixture becomes too high to achieve adequate stirring.

Two solvents, toluene and methylcyclohexane have been used for the polymerization. Polymers prepared in each of these solvents are essentially the same, as illustrated in Table XXII. Cyclohexane is often described as a solvent for preparing anionic CTPB in patents issued to workers at Phillips Petroleum Company. This solvent has not been examined as yet, since it was felt that its relatively high melting point would present difficulties in carbonating the polymers.

TABLE XXII. EFFECT OF SOLVENT ON ANIONIC CTPB .

Run No.	Solvent	Fraction	Wt. % of Total Polymer	\bar{M}_n^{cor}	\bar{M}_{acid}	Function- ality	$\langle\eta\rangle$	Over-all Function- ality (calc.)
18557-37	toluene	low MW fraction	35	1600	620	2.6	0.07	2.1
		high MW fraction	65	4700	2830	1.6	0.18	
18557-39	methylcyclo- hexane	low MW fraction	40	1700	660	2.6	0.07	2.0
		high MW fraction	60	3850	3250	1.2	0.23	

Carbonation Procedure. — As discussed previously, the carbonation procedure employed to convert dilithiopolybutadiene to CTPB can result in chain extension through reaction of lithium alkyl groups with lithium carboxylate moieties. For this reason, it is felt that the concentration of carbon dioxide should always be much greater than the concentration of lithium terminated polymer throughout the carbonation reaction. The usual method of effecting carbonation of the polymers has been to pressure a solution of the dilithiopolybutadiene on to excess solid carbon dioxide at -78°C. The dilithiopolybutadiene solution, which is very viscous, becomes gelatinous upon contact with the cold carbon dioxide and considerable time is required for complete reaction to occur as judged by the disappearance of the characteristic color of the original solution. Thus, it is possible that undesirable side reactions and chain extension reactions such as ketone and alcohol formation can occur during this step.

It was attempted to improve the carbonation procedure by adding the polymer solution to a saturated solution of carbon dioxide in methylcyclohexane. Data for two such runs are shown in Table XXIII. This carbonation technique did not seem to offer any advantages over

carbonation by solid carbon dioxide since the polymer solution also formed a gel when contacted with the solution of carbon dioxide. These polymers also exhibited the broad distribution of molecular weights and functionalities observed in other runs. Later results indicated that the above methods of carbonation were inadequate and yielded polymers having broad molecular weight distributions. These results are discussed below under Molecular Weight Distribution.

It appears that the carbonation step is one of the most critical in the preparation of CTPB. It has been reported¹⁶ that the method of carbonation used has a pronounced effect upon the amount of carboxyl termination obtained in the resulting polymer and that the most effective method of carbonation involves mixing, under pressure, streams of the polymerization solution and gaseous carbon dioxide. It is planned to investigate this technique in the future.

TABLE XXIII. SOLUTION CARBONATION OF ANIONIC CTPB.

Run No.	Fraction	Wt. % of Total Polymer	\bar{M}_n^{cor}	\bar{M}_{acid}	Function- ality	$\langle \eta \rangle$	Over-all Function- ality (calc.)
18557-40	low MW fraction	40	1800	850	2.1	0.09	1.8
	high MW fraction	60	3600	2420	1.5	0.18	
18557-41	low MW fraction	50	1900	740	2.6	0.07	2.3
	high MW fraction	50	4850	2980	1.6	0.22	

Polymer Work-Up. — After carbonation, the polymer solution, which is in the form of a gel is treated with gaseous HCl to convert the lithium carboxylate groups to carboxylic acid groups. In many cases where the polymerization mixture contained some metallic lithium, it was necessary to add a small amount of water during the acidification step in order to convert the lithium to lithium chloride. If this was not done, the lithium reacted later in the workup and resulted in some of the carboxyl end groups being converted back to the salt structure. For example, in a typical run where water was not used, the final polymer was found to be only partially soluble and to have an acid equivalent weight of 17,000. After reacidification and repurification of the sample, it was found to be completely soluble and to have an acid equivalent weight of 4250. After acidification, the solvent is removed at reduced pressure and the polymer redissolved in ether and precipitated into alcohol in order to remove 2-methylnaphthalene. The alcohol is then decanted and the polymer dissolved in petroleum ether and Calco 2246 antioxidant added. The solvent is then removed and the polymer dried at reduced pressure using a rotary evaporator.

In many of the runs, it was found that a substantial portion of the polymer was soluble in isopropanol. In those cases, after precipitation, the isopropanol solution was distilled and the residual polymer subjected to steam distillation in order to remove 2-methylnaphthalene. It was then dissolved in petroleum ether, dried over CaSO_4 , antioxidant added and the solution centrifuged to remove any residual lithium chloride. Final drying of these fractions was accomplished as above. Data for typical runs in which an alcohol soluble fraction was obtained are listed in Table XXIV.

TABLE XXIV. ANIONIC CTPB CONTAINING ALCOHOL SOLUBLE FRACTION

Run No.	Fraction	Total Wt. % of Polymer	\bar{M}_n^{cor}	Acid Eq. Weight (\bar{M}_{acid})	Function- ality	$\langle\eta\rangle$	Over-all Function- ality (Calc.)
18557-29	low MW fraction	25	2200	970	2.3	0.09	1.6
	high MW fraction	75	3900	3040	1.3	0.20	
18557-36	low MW fraction	40	1700	605	2.8	0.07	2.2
	high MW fraction	60	3200	2350	1.4	0.17	
18557-37	low MW fraction	35	1600	620	2.6	0.07	2.1
	high MW fraction	65	4700	2830	1.6	0.18	

Molecular Weight Distribution. — The fact that many of the anionic polymerizations resulted in polymers partially soluble in alcohol indicated that the polymers had very broad molecular weight distributions and/or functionality distributions. This conclusion is supported by the data of Table XXIV which shows the low molecular weight, alcohol soluble fractions, to have considerably higher functionalities than the alcohol insoluble fractions. It was felt that one possible cause of these effects could be that initiation was being effected by more than one species, since the initiating mixture used contained some metallic lithium and lithium 2-methylnaphthalene complex in addition to the desired dilithiopolyisoprene initiator. Although metallic lithium and lithium 2-methylnaphthalene are insoluble in hydrocarbon solvents, they could, conceivably, still initiate polymerization of butadiene.

In order to eliminate the possibility of initiation by species other than dilithiopolyisoprene, a number of polymerizations were carried out in which the initiator solution was filtered prior to use. It was found that filtration gave a solution considerably lower in alkalinity than the unfiltered solution and that the amount of lithium in the filtered solution was only about half that expected based on the amounts of lithium and 2-methylnaphthalene used to prepare the initiator. Several different reaction conditions for preparation of the initiator were tried, but in all cases, the amount of lithium found in the final solution was considerably below the theoretical value. Data for these preparations are shown in Table XXV. A possible explanation of this effect is that the reaction of isoprene with the lithium 2-methylnaphthalene complex results in a fairly broad molecular weight distribution of the dilithiopolyisoprene initiator and that a significant amount of the initiator is in the form of very short chains which are insoluble in hydrocarbon solvents. In future work, dienes other than isoprene will be used for preparing the initiator solution in an attempt to make the reaction more efficient.

Data for some typical polymerizations utilizing a filtered initiator solution are shown in Table XXVI. These polymers did not contain an appreciable alcohol soluble fraction indicating that more than one type of initiator had been involved in previous runs. However, the molecular weight distributions of these polymers were found to be still very broad by gel permeation chromatography.

TABLE XXV

Preparation of Dilithiopolyisoprene Initiator Solution

Run No.	Ether (ml.)	Reaction time of Li (.058 g.-atom) + 2-Methylnaphthalene (.026 mole) in Ether (hr.)	Isoprene (g.)	Reaction time of Isoprene (min.)	Total Equivalents Lithium in Final Solution
45-4	25	24	—	—	0 (control)
45-1	25	24	4.3	30	0.012
45-2	25	48	4.3	30	0.012
45-3	50	24	4.3	30	0.013
45-6	25	24	4.3	10	0.008
46-1	25	24	2.9	10	0.007
45-7	25	24	4.3	30	0.015

TABLE XXVI

Preparation of Anionic CTPB using Filtered Initiator Solution

Run No.	Acid Eq.	$\langle \eta \rangle$	$M_n^{(corr)}$	Functionality
18557-42	14,200	0.64	25,000 (membrane osmometry)	1.8
18557-48	6300	0.44	10,000	1.6
18557-51	3320	0.27	5500	1.7

As discussed previously, the carbonation procedure can lead to CTPB having a broad molecular weight distribution. In order to determine if this was occurring in the anionic polymerizations, runs were carried out in which a portion of the polymerization reaction was reacted with methanol to give hydride termination while the remainder was carbonated in the usual manner. Comparison of the viscosities of the two types of polymer indicated the carboxylated material to be of considerably higher molecular weight. Gel permeation chromatography indicated the hydrogen-terminated polymers to have a fairly narrow molecular weight distribution while the carboxyl-terminated polymers had a very broad distribution. These effects are shown in Table XXVII. The fact that the hydrogen-terminated polymers have a quite narrow molecular weight distribution indicates that the polymerization techniques used are capable of producing satisfactory CTPB since if impurities were present or termination reactions were occurring during the polymerization, one would expect the hydrogen-terminated polymer to have a broad molecular weight distribution.

In an attempt to improve the carbonation procedure, the following techniques were tried:

- 1) Addition of ether to the polymerization reaction to reduce the viscosity.
- 2) Dilution of the polymerization reaction prior to carbonation.
- 3) Addition of ether to both the polymerization reaction and the carbonation reactor.

The above techniques still resulted in carboxyl-terminated polymers having molecular weights considerable different from their corresponding hydrogen-terminated polymers, as indicated by viscosity measurements. These results are shown in Table XXVIII. It has been reported¹⁶ that the most effective method of carrying out the carbonation procedure is to blend a stream of the polymerization solution with gaseous carbon dioxide under pressure. This technique will be tried in future work.

TABLE XXVII

Molecular Weight Distributions of Carboxyl- and Hydrogen-Terminated Polybutadiene

Run No.	$\langle \eta \rangle$	A_w/A_n (gel permeation chromatography)
18557-53		
H-terminated	0.16	1.3
CO ₂ H-terminated	0.24	6.8
18557-54		
H-terminated	0.16	1.3
CO ₂ H-terminated	0.22	5.4

TABLE XXVIII

Effect of Different Carbonation Procedures on MW Distribution of Anionic CTPB.

Run No.	Carbonation Technique	$\langle \eta \rangle$
18557-54		
H-term.	Polym. rx. pressured onto solid CO ₂ (control run)	0.16
CO ₂ H-term.		0.22
20546-4		
H-term.	Added 5% ether to polym. rx. before carbonation.	0.11
CO ₂ H-term.		0.17
20546-5		
H-term.	Added 5% ether to polym. rx. and carbonation reactor	0.12
CO ₂ H-term.		0.22
20546-7		
H-term.	Diluted polym. rx. with equal volume of methyl-chlohexane before carbonation	0.13
CO ₂ H-term.		0.26

MICROSTRUCTURE OF ANIONIC CTPB

The microstructures of some typical polymers prepared by anionic techniques are shown in Table XXIX. The values obtained in the structure of the polymer prepared using dilithio-polyisoprene as initiator are quite similar to those obtained on the commercial anionic polymers using the same analytical method.

TABLE XXIX. Microstructure of Anionic CTPB.

	% Cis-1,4	% Trans-1,4	% Vinyl
Lithium-naphthalene in THF (16957-44)	3	7	97
Dilithiotetraphenylethane in THF-ether	19	15	74
Dilithiopolyisoprene in toluene	21	31	42
Phillips Petroleum Company (Butarez CTL-2)	24	35	37
General Tire and Rubber Company (Telegan Liquid Rubber)	27	38	36

C. POLYMER CHARACTERIZATION

General Considerations

During most of the period covered by this report, the synthetic aspects of CTPB were emphasized with only "routine" analyses such as infrared, inherent viscosity, molecular weight and acid equivalent weight being run on the polymers. As the program progressed, it became apparent that the characterization of CTPB presented a number of difficulties, particularly in regard to the determination of molecular weights (and thus functionalities) and inherent viscosities. The absolute values of these quantities reported in the previous sections are therefore probably not accurate but are useful for comparing different samples of CTPB prepared by similar techniques. Later in the program a more fundamental study of the characterization of CTPB was started and will be continued in future work. The polymers used for this initial characterization study comprised the four commercially available polymers and a representative 3M polymer. These polymers are listed in Table XXX.

TABLE XXX. Polymers Used for Characterization Studies.

Sample No.	Description
16957-39-A	General Tire and Rubber Company, Talagen Liquid Rubber 596-720
16957-39-G	Goodrich Hycar CTB, Lot 13
16957-39-P	Phillips CTL-2, Lot 303
18974-49-T	Thiokol HC-434, Lot 30 M
18974-31-5E	3M azo-initiated

Polymer Fractionation. —In addition to the above samples, data was also obtained on fractions derived from samples 18974-49-T and 18974-31-5E. The fractionations were carried out by coating the polymers on glass beads and eluting the column with CHCl_3 -methanol mixtures. Approximately ten gram quantities of each polymer were fractionated in this manner with individual fractions being of the order of 0.5g.

Gel Permeation Chromatography. —The polymers were examined by gel permeation chromatography in THF and chloroform using a Waters instrument. From the curves obtained, the quantities A_n (number average backbone length), A_w (weight average backbone length) and the ratio A_w/A_n (a measure of the broadness of the distribution of the polymer) were calculated. In all calculations, materials below 15 Å backbone length were excluded.

Aging characteristics of the whole polymers in THF and CHCl_3 solutions were first examined. Solution of 1% polymer were prepared and analyzed by GPC at intervals over a period of one month. The solutions were stored at room temperature and exposed to light only when withdrawing a sample. The results were the same in both solvents. None of the polymers showed any significant changes upon aging in solution. The results are shown in Tables XXXI and XXXII.

The fractions prepared by elution techniques were also analyzed by gel permeation chromatography. It was hoped that the A_w/A_n ratios of these fractions would be low indicating successful fractionation based on molecular weight differences. However, it was found that the fractions were quite broad, giving A_w/A_n ratios ranging from 1.8 up to 3.0 when the solutions were less than one day old. Further investigation showed a similar behavior during runs on whole polymers when samples were run immediately after preparation. The

weight averages did not show much fluctuation but number averages increased considerably.

Figure 9 shows a typical plot as derived, illustrating this effect. This problem is different from the one studied in the aging test where the main concern was changes occurring over a larger period such as a month. The reason for this anomalous short term aging effect may be due to changes occurring in the GPC columns and will be investigated further.

Viscosity. — In most of the work under this contract, inherent viscosities of polymers have been measured in benzene solutions. With many of the polymers prepared, these inherent viscosities have been assumed to be close approximations to intrinsic viscosities and have been used to estimate viscosity-average molecular weights. Molecular weights calculated from viscosities in toluene have also been reported by other workers.⁸

Recently a more intensive investigation of solution viscosities of CTPB was started. Inherent and reduced specific viscosities of the above samples were determined at several concentrations using a Cannon-Ubbelohde micro dilution viscometer. These were extrapolated to zero concentration to yield intrinsic viscosities. A typical plot is shown in Figure 10. As can be seen, an unusual drop in viscosity was noted at lower concentrations which may be attributed to intermolecular association at higher concentrations. The intrinsic viscosity of sample 18974-49-T was determined in benzene ($[\eta] = 0.21$) as well as in toluene ($[\eta] = 0.18$) showing that these two solvents are not comparable.

TABLE XXXI. GPC DATA FOR CTPB SAMPLES AFTER AGING IN CHCl_3 .

Polymer	Solution Age (Days)	A_n	A_w	A_w/A_n	Run Number
16957-39-A	3	81	235	2.90	1056
16957-39-A	7	84	217	2.59	1071
16957-39-A	30	88	225	2.60	1195
16957-39-G	7	65	155	2.38	1072
16957-39-G	30	71	185	2.62	1194
16957-39-P	7	95	300	3.16	1074
16957-39-P	30	85	372	4.38	1143
18974-49-T	0	74	167	2.25	1063
18974-49-T	2	62	126	2.04	1050
18974-49-T	5	65	161	2.48	1059
18974-49-T	30	81	196	2.42	1188
18974-31-5E	0	82	210	2.56	1081
18974-31-5E	30	81	266	3.28	1205

TABLE XXXII. GPC DATA FOR CTPB SAMPLES AFTER AGING IN THF

Polymer	Solution Age (Days)	A_n	A_w	A_w/A_n	Run Number
16957-39-A	1	66	196	2.97	1011
	3	77	227	2.94	1023
16957-39-G	1	65	145	2.24	1010
	3	71	159	2.24	1024
16957-39-P	1	81	274	3.38	1009
	9	95	276	2.90	960
	24	69	255	3.70	1022
18974-49-T	1	75	200	2.67	1012

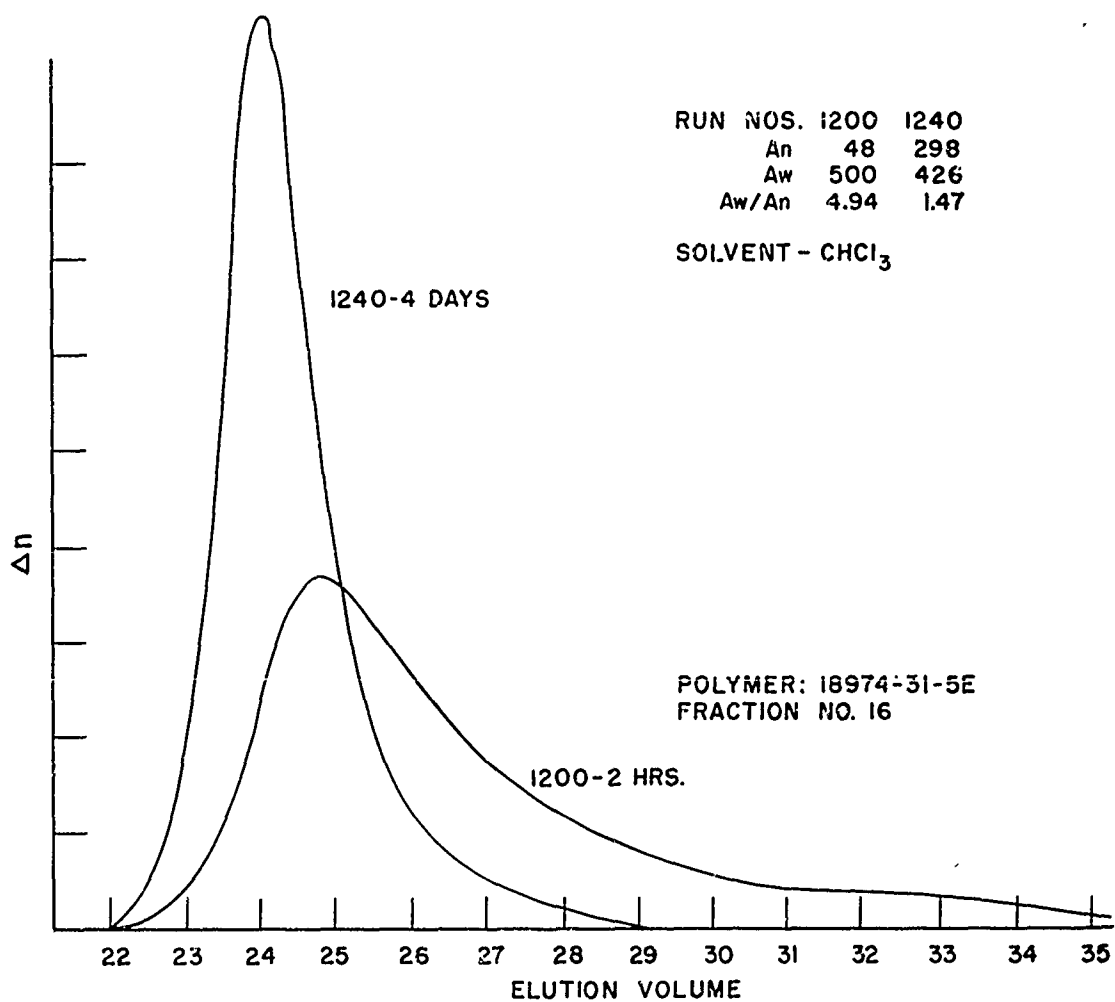


FIGURE 9. Change in GPC CURVES With Time for CTPB.

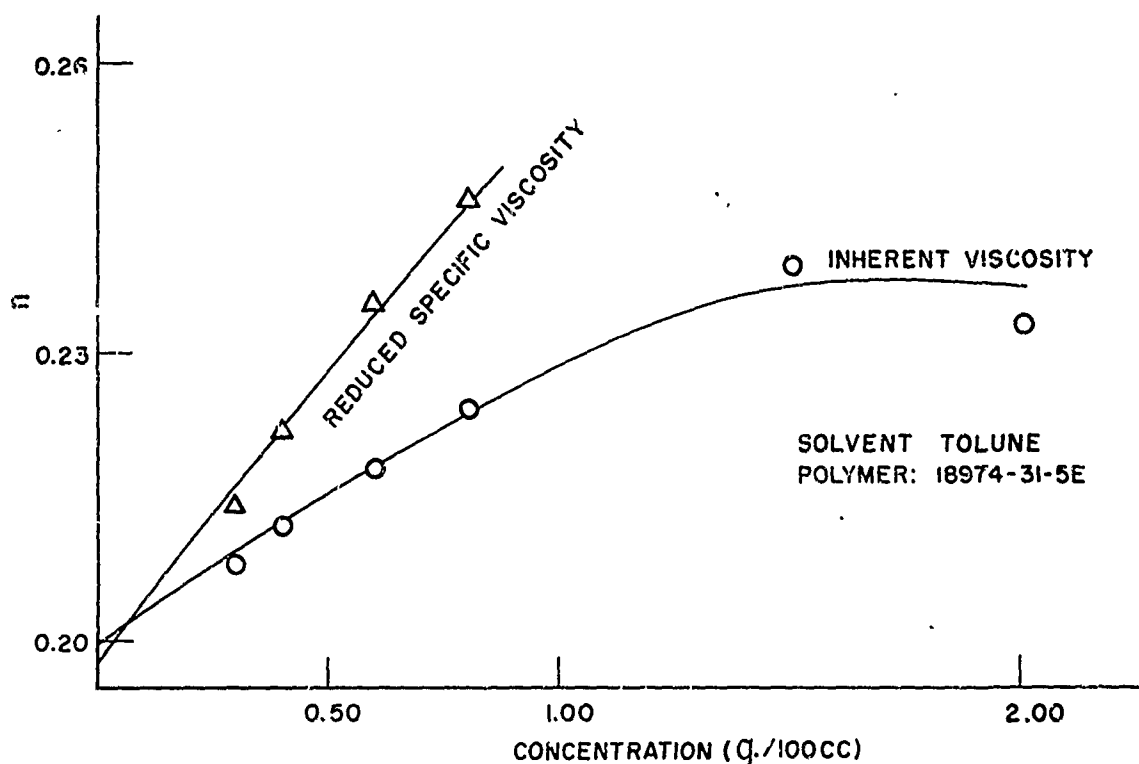


FIGURE 10. Inherent and Reduced Specific Viscosities VS Concentration for CTPB.

A summary of the viscosity data obtained is given in Tables XXXIII and XXXIV. Because of the apparent association noted, it is felt that molecular weights calculated from inherent viscosity data should only be used to give relative values of molecular weight when comparing similar samples of the same type of CTPB and should not be considered as accurate molecular weight determinations.

It would be desirable to run viscosity determinations in a solvent which does not show a dependence upon concentration as noted for benzene and toluene. This would permit the use of inherent viscosity measurements for estimation of molecular weights rather than intrinsic viscosities which require considerably more time to determine. Future work will involve the investigation of viscosities in other solvents.

Molecular Weight Measurements. — Perhaps the greatest problem associated with the characterization of carboxyl-terminated polybutadiene is the determination of number-average molecular weight. This value is, of course, important for the determination of functionality of the polymer. Number-average molecular weights in the range of interest for CTPB samples are commonly determined by vapor pressure osmometry. The problems connected with this determination may be divided into three areas:

- 1) Instrument reliability
- 2) Sample impurities and
- 3) Solvent effects.

TABLE XXXIII. VISCOSITY DATA FOR CTPB WHOLE POLYMERS

Solvent: Toluene

Polymer	$[\eta]$
16957-39-A	0.15
16957-39-G	0.21
16957-39-P	0.19
18974-49-T	0.19
18974-31-5E	0.20

TABLE XXXIV. VISCOSITY DATA FOR CTPB FRACTIONS.

Solvent: Toluene

Polymer	Fraction No.	Cumulative Wt. %	$[\eta]$
18974-49-T	4	7	0.08
	8	18	0.10
	12	33	0.13
	15	53	0.18
	18	72	0.23
	22	94	0.34
18974-31-5E	7	15	0.09
	11	32	0.13
	13	54	0.19
	16	83	0.28
	20	96	0.46
	21	100	0.53

It has been noted that repeated molecular weight determinations on the same sample often show a considerable deviation and that results can vary depending upon the standard used for calibration of the VPO instrument. It is estimated that the possible error in the instrument is of the order of at least 5-10% at the lowest molecular weights and becomes much greater at the higher molecular weights.

The severe effect impurities have on number-average molecular weight can be shown by the following example. A 1% concentration of Calco 2246 of MW = 340 causes about 2% lowering of the observed value for $\bar{M}_n = 1000$ but 20% lowering for $\bar{M}_n = 5000$ and 40% for $\bar{M}_n = 20,000$. To eliminate the effect of impurities on the determination of \bar{M}_n for CTPB, two possibilities exist. All of the impurities could be determined and the appropriate corrections made, a very difficult and time consuming procedure; or, the impurities could be removed by some procedure such as precipitation of the polymer into a non-solvent. The latter method is much simpler; however the procedure invariably removes some very low molecular weight polymer and thus does not yield a truly representative sample.

Since some evidence for association effects in non-polar solvents was obtained by viscosity measurements, it might be expected that effects of this type would also be present in VPO molecular weight measurements, and that polar solvents would be more suitable.

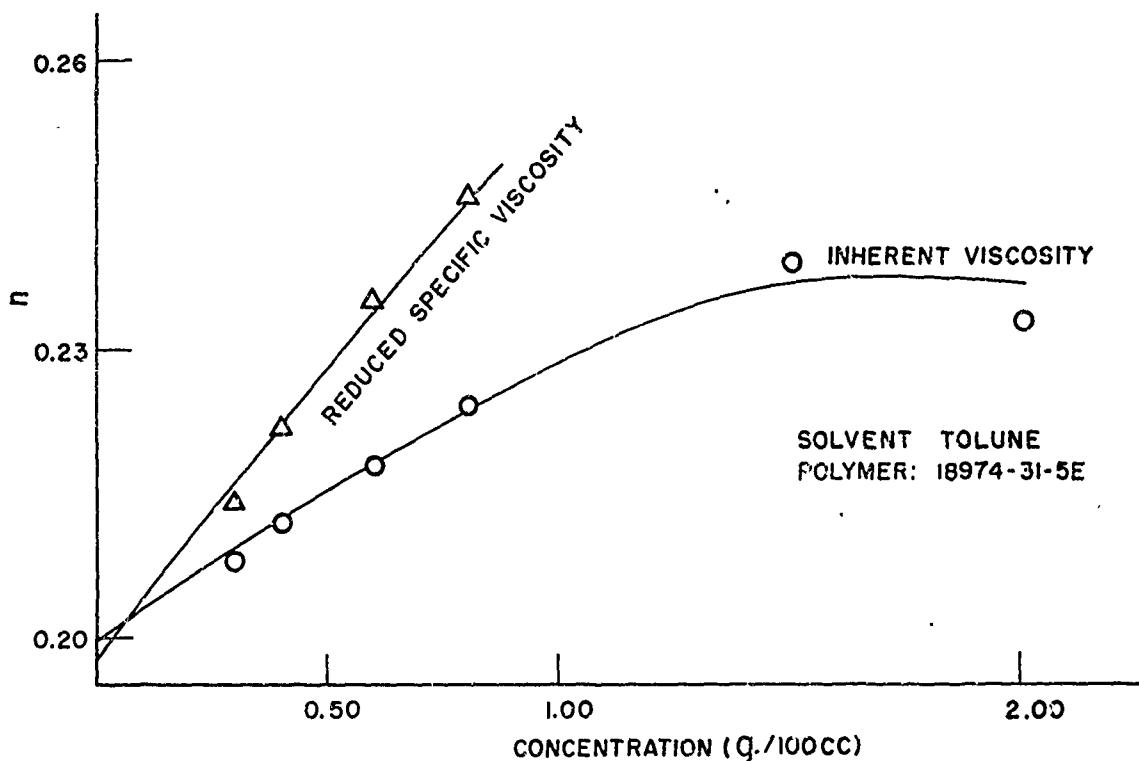


FIGURE 10. Inherent and Reduced Specific Viscosities VS Concentration for CTPB.

A summary of the viscosity data obtained is given in Tables XXXIII and XXXIV. Because of the apparent association noted, it is felt that molecular weights calculated from inherent viscosity data should only be used to give relative values of molecular weight when comparing similar samples of the same type of CTPB and should not be considered as accurate molecular weight determinations.

It would be desirable to run viscosity determinations in a solvent which does not show a dependence upon concentration as noted for benzene and toluene. This would permit the use of inherent viscosity measurements for estimation of molecular weights rather than intrinsic viscosities which require considerably more time to determine. Future work will involve the investigation of viscosities in other solvents.

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	18	72	0.23
	22	94	0.34
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	11	32	0.13
	13	54	0.19
	16	83	0.28
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	21	100	0.53

It has been noted that repeated molecular weight determinations on the same sample often show a considerable deviation and that results can vary depending upon the standard used for calibration of the VPO instrument. It is estimated that the possible error in the instrument is of the order of at least 5-10% at the lowest molecular weights and becomes much greater at the higher molecular weights.

The severe effect impurities have on number-average molecular weight can be shown by the following example. A 1% concentration of Calco 2246 of MW = 340 causes about 2% lowering of the observed value for $\bar{M}_n = 1000$ but 20% lowering for $\bar{M}_n = 5000$ and 40% for $\bar{M}_n = 20,000$. To eliminate the effect of impurities on the determination of \bar{M}_n for CTPB, two possibilities exist. All of the impurities could be determined and the appropriate corrections made, a very difficult and time consuming procedure; or, the impurities could be removed by some procedure such as precipitation of the polymer into a non-solvent. The latter method is much simpler; however the procedure invariably removes some very low molecular weight polymer and thus does not yield a truly representative sample.

Since some evidence for association effects in non-polar solvents was obtained by viscosity measurements, it might be expected that effects of this type would also be present in VPO molecular weight measurements, and that polar solvents would be more suitable.

Number-average molecular weights for the various CTPB samples were determined by vapor pressure osmometry in four different solvents. The data are shown in Table XXXV. The corrected values are corrected only for antioxidant content using the quantities in Table XXXVI. The values obtained in CHCl_3 and THF were, in general, very similar and in almost all cases considerably lower than the values obtained in benzene and MEK. The MEK results are somewhat surprising since association in this solvent would be expected to be much less than in benzene and has been reported⁸ to be the solvent of choice for VPO measurements of CTPB by other workers. Since corrections were made only for antioxidant content, it may be assumed that the values obtained in CHCl_3 and THF are too low. It was noticed that all of the polymers contained some volatile impurities and that the samples lost weight when subjected to low pressure (100 μ) for 24 hours.

Another variable in the determination of \bar{M}_n for CTPB is sample homogeneity. To test the homogeneity of the polymers, sample 16957-39-A was sampled four times (from different parts of the container) and \bar{M}_n values determined. An additional four samples were then taken, combined in solution and four determinations of \bar{M}_n made. The spread in these values was much less. The data are shown in Table XXXVII. These results suggest that samples of CTPB contain a low molecular weight impurity which is not uniformly dispersed.

Future work will involve more study on the nature and quantities of low molecular weight impurities present in CTPB and methods of removing these before running \bar{M}_n determinations.

Functionality. — It would be highly desirable to be able to obtain accurate values for the functionality (no. of acid groups/molecule = \bar{M}_n /Acid Eq. Wt.) of CTPB since this number is an indication of the amount of crosslinking that can be achieved in the polymer. However, at the present time, there appears to be considerable uncertainty in the functionality values due to the difficulties involved in determining number-average molecular weights.

TABLE XXXV. \bar{M}_n VALUES BY VPO FOR CTPB SAMPLES

Standard: Sucrose Octaacetate

Solvent	Polymer				
	16957-39-A	16957-39-G	16957-39-P	18974-49-T	18974-31-5E
Chloroform	2800(3700)	3100(3600)	2200(2400)	2900(3500)	2900 (3600)
Tetrahydrofuran	3100(4000)	3100(3600)	2300(2500)	3100(3600)	3200 (4100)
Benzene	4000(5800)	5400(7400)	3100(3500)	5600(7400)	3400 (4300)
Methyl ethyl ketone	4500(6900)	4400(5600)	3400(3900)	4800(6100)	-----

Figures in parentheses are corrected for antioxidant content.

TABLE XXXVI. ANTIOXIDANT CONTENTS OF CTPB SAMPLES

Polymer	Antioxidant	%	Method of Determination
16957-39-A	Calco 2246	2.8	U.V. Spectroscopy
16957-39-G	Calco 2246	1.8	U.V. Spectroscopy
16957-39-P	Calco 2246	1.5	Titration
18974-49-T	Phenyl-B-naphthylamine	1.0	U.V. Spectroscopy
18974-31-5E	Calco 2246	2.4	Amount added

TABLE XXXVII. \bar{M}_n Values of CTPB, Before and After Blending Polymer: 16957-39-A

Sample as Received	After Blending
5240	5900
4270	6000
5340	5800
2850	7000

Table XXXVIII lists functionality numbers for several CTPB samples calculated from \bar{M}_n values in different solvents. The CHCl_3 and THF results generally agree quite well while the benzene and MEK values are much higher and quite erratic in their relationship to each other which may be due to association effects. For most of the samples, the values in CHCl_3 and THF are much too low, if one assumes the polymers have functionalities close to two. This may be due to the presence of low molecular weight impurities, other than antioxidant, in the polymers. No correction was made for these impurities. In some cases the benzene and MEK results would appear to be reasonable while in other cases they seem to be too high. This is probably the result of association effects (causing high results) being somewhat balanced by impurity effects (causing low results).

TABLE XXXVIII. FUNCTIONALITIES OF CTPB SAMPLES

Polymer	Acid Eq. Wt.	Solvent	$\bar{M}_n^{(\text{cor})}$	Functionality
16957-39-A	2800	CHCl_3	3700	1.3
		THF	4000	1.4
		C_6H_6	5800	2.1
		MEK	6900	2.5
16957-39-P	2800	CHCl_3	2400	0.9
		THF	2500	0.9
		C_6H_6	3500	1.3
		MEK	3900	1.4
16957-39-G	2400	CHCl_3	3600	1.5
		THF	3700	1.5
		C_6H_6	7400	3.1
		MEK	5600	2.3
18974-49-T	1900	CHCl_3	3500	1.8
		THF	3600	1.9
		C_6H_6	7400	3.9
		MEK	6100	3.2
18974-31-5E	2200	CHCl_3	3600	1.6
		THF	4100	1.9
		C_6H_6	4400	2.0
		MEK	—	—

The dependence of functionality on molecular weight was investigated for the fractionated polymers. Functionalities of the individual fractions were calculated from number-average molecular weight values obtained in THF and also from viscosity-average molecular weights calculated as shown in Table XXXIX. Plots of functionality vs. cumulative wt. per cent for the two polymers are shown in Figures 11 and 12. Both plots tend to rise as molecular weight increases until a certain point is reached and then functionality, as determined by either method, falls off sharply. Some of this effect may be due to inaccuracies in molecular weight measurements at higher molecular weights; however, the fact that the same effect is noted for both types of molecular weight measurements suggests that functionality is decreasing at the highest molecular weights. This effect will be investigated further with other polymer samples.

Plots of Acid Eq. Wt. vs. cumulative percentages for the two fractionated polymers are shown in Figures 13 and 14. The rather sharp breaks in the curves at higher molecular weights again suggests differences in functionality for different fractions. This effect will also be studied with other polymers.

TABLE XXXIX. VISCOSITY-AVERAGE MOLECULAR WEIGHTS
FOR CTPB FRACTIONS

Calculated from relationship* $[\eta] = 8.0 \times 10^{-4} \bar{M}_v^{0.62}$

Polymer	Fraction No.	Cumulative Wt. %	in toluene	\bar{M}_v
18974-49-T	4	7	0.08	1,660
	8	18	0.10	2,350
	12	33	0.13	3,640
	15	53	0.18	6,040
	18	72	0.23	9,220
	22	94	0.34	17,000
18974-31-5E	7	15	0.09	2,000
	11	32	0.13	3,640
	13	54	0.19	6,460
	16	83	0.28	12,600
	20	96	0.46	27,600
	21	100	0.53	34,700

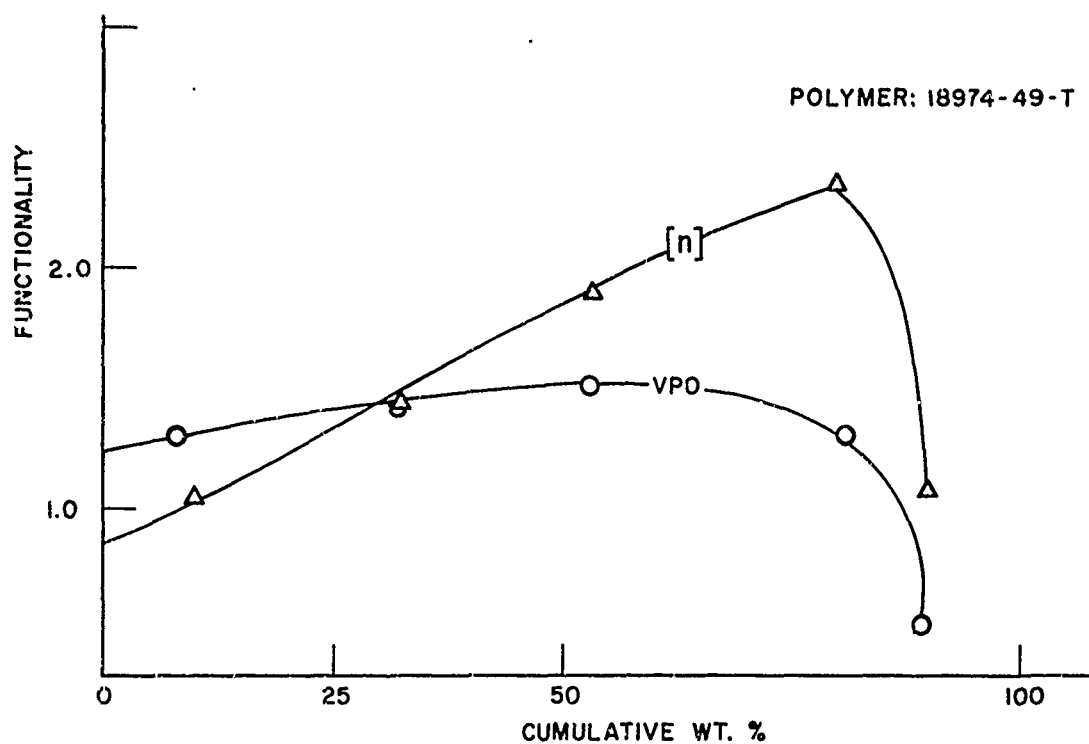


FIGURE 11. Functionality VS Cumulative Weight Percent For Fractionated CTPB

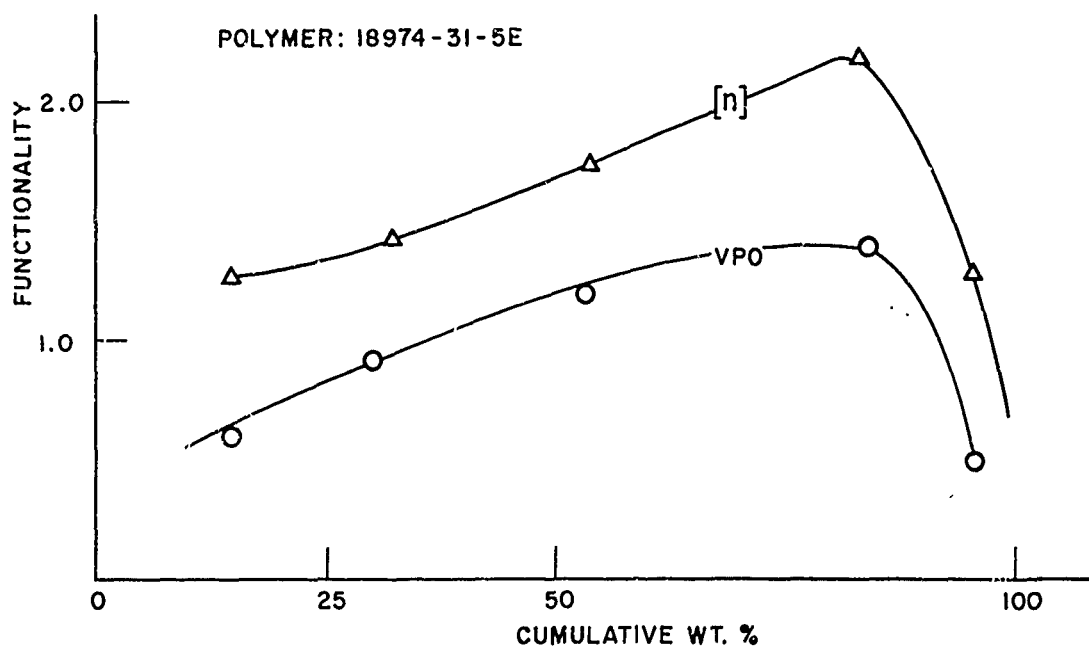


FIGURE 12. Functionality VS Cumulative Weight Percent For Fractionated CTPB

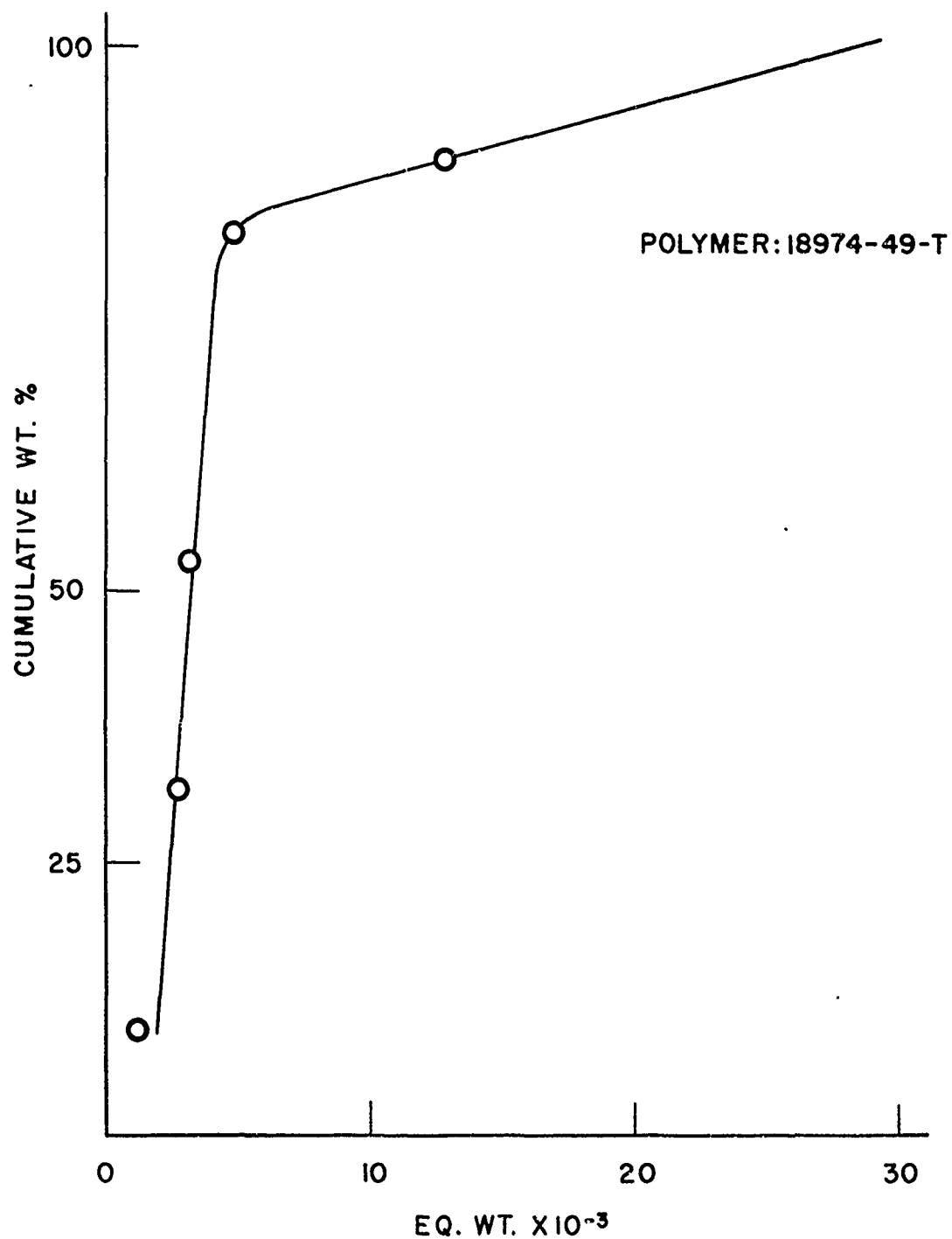


FIGURE 13. Acid Eq. Wt. VS Cumulative Weight Percent For Fractionated CTPB

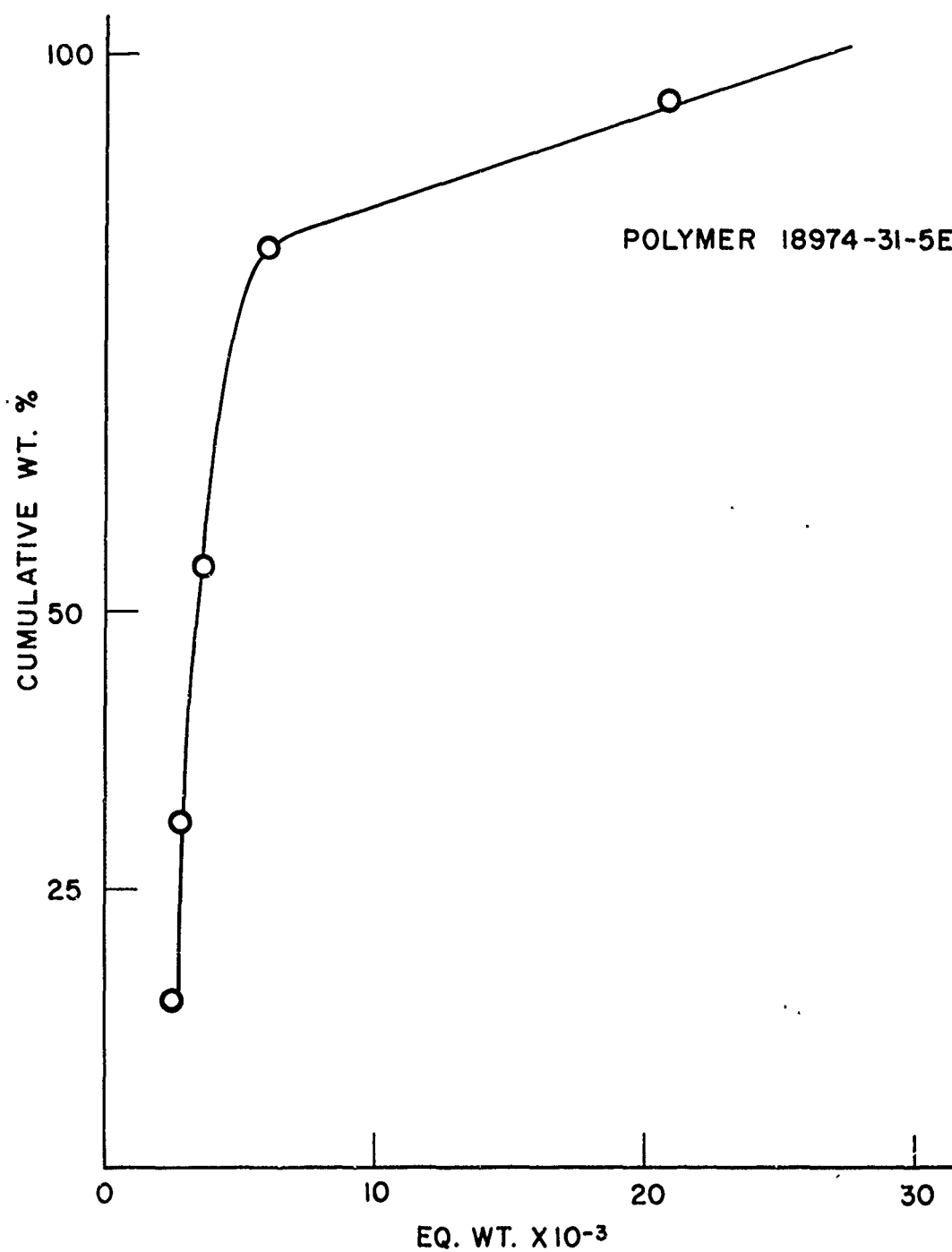


FIGURE 14. Acid Eq. Wt. VS Cumulative Weight Percent For Fractionated CTPB

III. EXPERIMENTAL

A. RADICAL POLYMERIZATION

Preparation of Glutaric Acid Peroxide. In a 600-ml. beaker equipped with a magnetic stirring bar was placed 100 g. (0.885 mole) of glutaric anhydride. To this was added slowly with stirring 87.5 cc. of 30% hydrogen peroxide (0.86 mole) diluted to 350 cc. with water. Stirring was continued at room temperature for 1 hour after the addition was complete. The clear solution began to turn cloudy after about 30 minutes and at the end of the stirring period a precipitate had separated. The mixture was stored in the refrigerator overnight. The next morning it was filtered while still cold, and the precipitate was washed sparingly with water and air-dried. The yield of white, crystalline product was 31.5 g. (28%)

Anal. Calcd. for $C_{10}H_{14}O_8$: equiv. wt. at 1st break, 131; at 2nd break, 87; percent active oxygen, 12.2. Found: equiv. wt. at 1st break, 124; at 2nd break, 80; percent active oxygen, 11.9.

Free Radical Ampoule Runs. — The small scale radical polymerizations were carried out in 60-cc. glass ampoules. The solvent and initiator (and chain transfer agent in certain runs) were charged and the resulting mixture cooled in a -196° bath. The ampoule was then evacuated to $<10^{-1}$ mm., and the contents put through three cycles of thawing, freezing, and evacuating to remove any entrapped oxygen. The butadiene, which had previously been metered into the vacuum system in correct amount, was condensed into the ampoule and the ampoule sealed. The ampoules were heated in a hot rocker, the contents removed, antioxidant added, and the solution allowed to evaporate to dryness. The residue was extracted with benzene (sometimes cyclohexane), the extract filtered, and the filtrate evaporated to dryness to yield the polymer. The products were viscous liquids, which, in general, were very light colored, but in the case of succinic acid peroxide runs a very dark brown.

Preparation of One-Pound Lots of CTPB. — The equipment used is shown in Figure 2.

Reaction Procedure

1. Make up desired activator solution.
2. Add 100 ml. solvent to evacuated, dry, clean reactor through activator feed system.
3. Charge activator solution into the 2-liter separatory funnel. Start pump and pump injection system to desired operating pressure as determined by the back pressure regulator setting (350 psig). Then top-out activator solution in the 2-liter separatory funnel to desired level (1000 ml.)

Note: The activator solution should be filtered during charging to 2-liter vessel.

4. Start coolant water to injection nozzle and top bearing of agitator.
5. Start agitator and start liquid N_2 cooling through internal coils.
6. Connect butadiene cylinder to unit. When reactor is $<0^\circ C.$ and $\sim 27"$ Hg start butadiene addition. Record — take weight; start heating tape on butadiene cylinder.
7. Record gross weight after desired charge and close butadiene charging valves.
8. Stop liquid N_2 and set jacket valves for steam use. Keep the steam inlet valve on the jacket closed.

9. Turn on steam (before regulator and valve) and open all valves up to the reactor jacket inlet valve. Have steam pressure <30 psig.
10. Open steam valve on reactor jacket. Readjust steam pressure to 10 psig. when the reactor temperature reaches 120°C.
11. Record time, temperature, and pressure, and start activator solution feed at desired feed rate.
12. Check addition rate, temperature, and pressure every 5-10 minutes to maintain linear addition rate.
13. After desired amount of activator has been added, shut off activator feed system (pump and valve) and let reactor run for 5 minutes to allow the last increment of activator to react.
14. Shut off steam. Have 3-liter flask receiver in place in portable hood. Turn on cooling water. Have enough antioxidant in receiver flask to yield 10 grams antioxidant/lb. of polymer.
15. Start dumping product at 90°C. or 150 psig. When pressure reaches 0 psig. open valve all the way.
16. Let reactor drain overnight.

Product Work-up Procedures

1. Using GAP activator and THF solvent (high MW polymer, 5000) –
 - A. Strip THF on rotary evaporator.
 - B. Wash polymer with 1000 cc. of isopropyl alcohol. This is done in the 3-liter flask that the product was dumped in, and the THF stripped from. Add this alcohol mixture to 2-liter separatory funnel.
 - C. Dissolve remaining polymer in 1000 cc. of CCl₄ and then add this to the 2-liter separatory funnel containing the isopropanol mixture.
 - D. Vigorously mix the two layers and allow about 4 hours for separation to occur.
 - E. Draw off the bottom, CCl₄-polymer layer and filter it with a 25-50 μ fritted disc filter using vacuum.
 - F. Strip off CCl₄ on rotary evaporator.
2. Using ABCPA activator and THF solvent (High MW polymer, 5000) –
 - A. Strip THF.
 - B. Add 1-liter benzene to dissolve polymer.
 - C. Filter the benzene-polymer solution using a 25-50 μ fritted disc filter under vacuum.
 - D. Strip benzene from filtrate.
3. Low MW polymer (2500) in THF with GAP or ABCPA –
 - A. Strip THF.
 - B. Add 1 liter cyclohexane.
 - C. Filter solution using 25-50 μ fritted disc filter.
 - D. If ABCPA is used go to next step. If GAP is used, strip the solution until ~200 ml. of cyclohexane is left; then filter this as per C.
 - E. Remove all cyclohexane from filtrate using rotary evaporator.

B. ANIONIC POLYMERIZATION

Materials

General: All reaction vessels were flamed out and cooled under argon just prior to use. Solid reagents were weighed out in a dry box under argon. Solvents and some solutions were charged using hypodermic syringes and serum stoppers. Syringes, tubing etc., were dried under vacuum at 100°, cooled in a dessicator and flushed with argon before use. When equipment was exposed to the atmosphere to make connections, the apparatus was immediately evacuated and flushed three times with argon. All distillations, purifications and reactions were run under a positive pressure of argon.

Lithium: 50% dispersion (in hexane) was used.

Stilbene and Tetraphenylethylene: Reagent grade materials were used without further purification.

2-Methylnaphthalene: Matheson, Coleman and Bell, m.p. 34-35°, used without further purification.

Ether: Ether was added slowly with stirring to LiAlH_4 (~.5 g./100 cc.) under argon and stirred for several minutes. Vacuum was then applied very briefly to remove air from the solvent. The ether was then distilled directly into the reaction vessel or into a storage container under argon.

Tetrahydrofuran: This solvent was purified by distillation from a solution of living polymer as described by Hayashi and Marvel.¹²

Isoprene: Isoprene was relaxed for 3 hours over freshly cut sodium, distilled into a receiver, evacuated briefly to degas and the storage vessel then filled with argon.

Methylcyclohexane and Toluene: Reagent grade solvents were passed through a column of silicagel and molecular sieve into a storage vessel containing sodium and degassed by pulling vacuum on the solvent for a short time.

Carbon Dioxide: Matheson, Coleman grade was used without further purification.

Butadiene: An initiator solution was prepared by reacting Li (1.2 g.), 2-methylnaphthalene (10.0 g.) and ethyl ether (75 cc.) for 16 hours and then adding isoprene (10 g.). Two cc. of this solution was added by means of a hypodermic syringe to refluxing butadiene (~50 g., Matheson Instrument grade) and the mixture stirred for 30 minutes. Butadiene was then distilled slowly into a cooled receiver collecting 20-25 g.

PREPARATION OF CTPB. – The following typical examples illustrate the preparation of CTPB by various anionic initiators.

Li-Naphthalene in THF. – A reaction flask was charged with lithium (0.3 g.) and resublimed naphthalene (6.1 g.) and tetrahydrofuran (275 cc.) distilled in. The mixture was stirred 16 hours at room temperature, cooled to -40° and butadiene (38 g.) distilled in over a period of 1 hour. After an additional 30 minutes reaction time, the extremely viscous solution was pressured onto solid carbon dioxide (~20 g.), resulting in gel formation. After warming to room temperature, the gel was acidified with dry HCl, Calco 2246 antioxidant (0.2 g.) added, and the solvent removed at reduced pressure. The polymer was then dissolved in benzene (200 cc.), centrifuged, the benzene distilled off and the polymer dried at 80-90°/1 mm. for 24 hours. Analysis of the resulting polymer (28 g.) gave the following values: $\langle\eta\rangle$, 0.18; Acid Eq. Wt., 6300; \bar{M}_n 3000; Microstructure (IR), 3% cis, 6% trans, 90% vinyl.

Li-Stilbene in THF-Toluene. — A 250 cc. flask was charged with lithium (1.1 g.), stilbene (9.0 g.), tetrahydrofuran (25 cc.) and ethyl ether (200 cc.) and the mixture stirred at room temperature for 16 hours. A 45 cc. portion of this solution was added to toluene (225 cc.) and the mixture subjected to vacuum until 40 cc. solvent had been removed. A very dark precipitate was present at this point. The mixture was warmed to 50° and butadiene (19 g.) distilled in. After stirring for 1 hour, the mixture was pressured onto carbon dioxide and allowed to warm to room temperature. Dry HCl was added and the mixture centrifuged to remove lithium chloride. Calco 2246 antioxidant (0.1 g.) was then added and the solvent removed and the polymer dried (60°/1 mm., 24 hours) on a rotary evaporator. The yield of polymer was 14.5 g. The following analytical results were attained: $\langle\eta\rangle$, 0.13; \bar{M}_n , 3000; Acid Eq. Wt., 4200; Microstructure, 18% cis, 15% trans, 66% vinyl.

Li-Tetraphenylethylene in THF-Toluene. — Tetraphenylethylene (3.44 g., 0.0104 moles) and lithium (0.4 g., 0.03 g. - atoms) were weighed into a 250 cc. flask. The flask was cooled to 0° and 5 cc. tetrahydrofuran and 75 cc. ethyl ether were distilled in. The reaction mixture was stirred 18 hours at room temperature resulting in formation of a dark red solution. This solution was charged into a 500 cc. reaction flask with 225 cc. toluene and the resulting mixture heated to 50°. A portion (80-90 cc.) of the solvent mixture was removed under reduced pressure. Butadiene (18.5 g., 0.342 moles) was then distilled in over a period of 15 minutes. After stirring for an additional hour at 50°, the reaction mixture was pressured onto 15-20 g. solid carbon dioxide, causing the solution to lose its color and become gelatinous. After warming to room temperature, the solution was acidified with dry HCl and centrifuged to remove LiCl. Calco 2246 antioxidant (0.1 g.) was then added, the solvent evaporated, and the polymer dried for 16 hours at 50°/1mm. on a rotary evaporator. At the end of this time the polymer was quite cloudy. It was dissolved in petroleum ether, and again centrifuged and dried. The insoluble portion consisted mainly of tetraphenylethylene. The polymer was found to have the following properties: $\langle\eta\rangle$, 0.12; Acid Eq. Wt., 2570; \bar{M}_n 2500; Microstructure, 19% cis, 15 trans, 74% vinyl; CO₂H absorbance, 0.112.

Dilithiopolyisoprene (Unfiltered). — A 500 cc. flask, fitted with a magnetic stirrer, Dry Ice condenser, dip tube, gas inlet, and distillation adapter was charged with lithium dispersion (0.6 g.), 2-methylnaphthalene (3.7 g.) and ethyl ether (25 cc.). The mixture was stirred at room temperature for 20 hours, cooled to -20° and isoprene (4.3 g.) added. The solution was allowed to warm to 0° over a period of 30 minutes and then toluene (225 cc.) was added and 30 cc. of solvent distilled off at reduced pressure. The mixture was then heated to 50° and butadiene (19 g.) distilled in over a period of 15 minutes. The mixture was stirred at 50° for an additional 45 minutes, during which time a large increase in viscosity was noted, and then pressured onto Dry Ice (~15-20 g.) causing immediate gelation of the polymer solution. This gel was allowed to warm to room temperature, acidified with dry hydrogen chloride, water (2 cc.) added, and the solvent removed at reduced pressure. The resulting crude polymer was dissolved in ethyl ether (50 cc.) and this solution added slowly, with vigorous stirring, to isopropanol (500 cc.). Most of the ether was removed from the resulting mixture by distillation at reduced pressure and the isopropanol decanted. The precipitated polymer was dissolved in petroleum ether (150 cc.) containing 0.200 g. Calco 2246 antioxidant, the solution centrifuged, the solvent removed at reduced pressure and the polymer dried 4 hours at 60°/1 mm. Addition of petroleum ether and drying was repeated three times, the final drying being for 24 hours. The resulting polymer had the following properties: \bar{M}_n^{cor} , 3200; Acid Eq. Wt., 2350; $\langle\eta\rangle$, 0.17; yield, 9.8 g.

The solvent was removed from the isopropanol solution at reduced pressure and the resulting polymer subjected to steam distillation until the odor of 2-methylnaphthalene was no longer

detectable in the distillate. Benzene was added to the polymer, the water phase separated and the benzene dried over CaSO_4 . Calco 2246 (0.100 g.) was then added, and the benzene distilled off. The polymer was then dissolved in petroleum ether, the solution centrifuged, and the polymer dried at $60^\circ/1$ mm. for 24 hours. The product was found to have the following properties: \bar{M}_n^{cor} , 1700; Acid Eq. Wt., 605; $\langle\eta\rangle$, 0.07; yield, 6.6 g.

Dilithiopolyisoprene (Filtered). — Lithium, 2-methylnaphthalene, ether and isoprene were reacted as described in the preceding example. Methylcyclohexane (200 cc.) was then added and solvent (47 cc.) distilled off at reduced pressure. The resulting mixture was filtered through a sintered glass filter into an evacuated 500 cc. reaction flask. A 5 cc. sample was withdrawn through a serum stopper by means of a hypodermic syringe and added to methanol (10 cc.). Titration of this solution with .1 N HCl, using phenolphthalein as indicator showed the solution of dilithiopolyisoprene in methylcyclohexane to contain 0.011 equivalents lithium. Butadiene (16 g.) was distilled into the initiator solution over a period of 5 minutes and the solution stirred at 25° for 90 minutes. Approximately half of the resulting viscous solution was pressured onto solid carbon dioxide and to the remainder was added methanol (10 cc.). The two polymer fractions were worked up by acidification, precipitation into isopropanol, etc., as described in the previous example. No alcohol soluble polymer was noted in either fraction. The following data were obtained for the carboxylated polymer: $\langle\eta\rangle$, 0.27; \bar{M}_n , 5500; Acid Eq. Wt., 3320; Microstructure, 25% cis, 35% trans, 40% vinyl; CO_2H absorption, 0.102. The following data was obtained on the hydrogen-terminated polymer: $\langle\eta\rangle$, 0.13; \bar{M}_n , 3100; Microstructure, 25% cis, 35% trans, 40% vinyl.

Carbocation of Dilithiopolyisoprene Initiator. — Lithium dispersion (0.50 g., .072 g.-atoms) and 2-methylnaphthalene (10.2 g., 0.012 moles) were weighed into a 250 cc. flask and ethyl ether (150 cc.) added by distillation. The mixture was stirred at room temperature for 16 hours, cooled to -20° and isoprene (12 g., 0.18 moles) added through a serum stopper. An immediate color change from purple to red-brown occurred upon addition of the isoprene. This solution (150 cc.) was added to toluene (200 cc.), the mixture stirred for 1 hour, and then pressured onto solid carbon dioxide. The resulting viscous solution was warmed to room temperature, acidified with dry HCl, filtered, and the solvent removed under reduced pressure. The polymer was then subjected to steam distillation until free of 2-methylnaphthalene, dissolved in benzene and the benzene solution dried over CaSO_4 . The rotary evaporator was used to remove the solvent and dry the polymer ($40^\circ/1$ mm. for 24 hours). The dried liquid polymer had the following properties: $\langle\eta\rangle$, 0.076; \bar{M}_n , 500; Acid Eq. Wt., 260; functionality, 1.9.

C. POLYMER CHARACTERIZATION

Infrared Analysis. — The determination of cis-trans-vinyl content of CTPB samples was done by infrared analysis using a Perkin-Elmer Model 521 Infrared Spectrophotometer. The wave numbers of the absorption bands used in these measurements are shown in Table XL.

TABLE XL.
INFRARED ABSORPTIONS USED TO CHARACTERIZE CTPB.

Group	Wave Length (cm. ⁻¹)
Vinyl	3070
	990
	906
Cis	720
Trans	962
Carboxyl	1705

The calibration polymer used was a sample of Thiokol Chemical Corporation CTPB (HC 434-Lot 19). The vinyl-cis-trans content of this polymer has been reported¹⁷ to be 30:22:49.

Acid Equivalent Weight. — Acid equivalent weights of CTPB were determined by dissolving the sample of polymer (0.5 to 1.0 meq. of carboxyl) in toluene (50 cc.), adding methanol (10 cc.) and tetrabutylammonium iodide (0.3 g.), and titrating with 0.1 N methanolic KOH. A Sargent Model 0 recording titrator with glass vs. Ag:AgCl combination electrode (using KCl saturated methanol as electrolyte) was used for the potentiometric titrations.

Molecular Weights. — Molecular weight measurements of CTPB samples were carried out using a Mechrolab Vapor Pressure Osmometer with sucrose octaacetate as the standard.

Fractionation Procedure. — Approximately 10 g. of the polymer were dissolved in methylene chloride (200 ml.) and the solution mixed with enough glass beads (120 μ diameter) to nearly fill a four foot column one inch in diameter (Figure 15). The solvent was evaporated and the coated beads were packed into the column and topped with approximately six inches of clean beads. Solvent was introduced into the column by means of two interconnecting reservoirs which made it possible to control solvent power of the elutant on a continuous basis.

Methanol (600 ml.) containing approximately 0.03% Calco 2246 antioxidant was introduced into the column and allowed to soak for 18 hours. This soaking helped to settle the column packing to eliminate "channelling" during the extraction. Methanol was then percolated through the column and collected in portions (200 ml.) at the bottom. The first fraction contained nearly all of the non-polymeric materials in the sample such as inhibitor, initiator fragments and some very heavily carboxylated polymeric materials.

Following elution by the methanol, 1500 ml. each of non-solvent (75% CH₃OH/25%CHCl₃) and solvent (25% CH₃OH/75%CHCl₃) were prepared, each containing 0.03% antioxidant. These were mixed and introduced into the column so that the solvent power of the elutant increased linearly. Fractions were collected as before. After the above solutions were exhausted, chloroform (1000 ml.) was added to remove all traces of polymer. The fractions were then evaporated to dryness at room temperature and weighed. Recoveries ranged from 96 to 100%. Analyses were then carried out on these fractions.

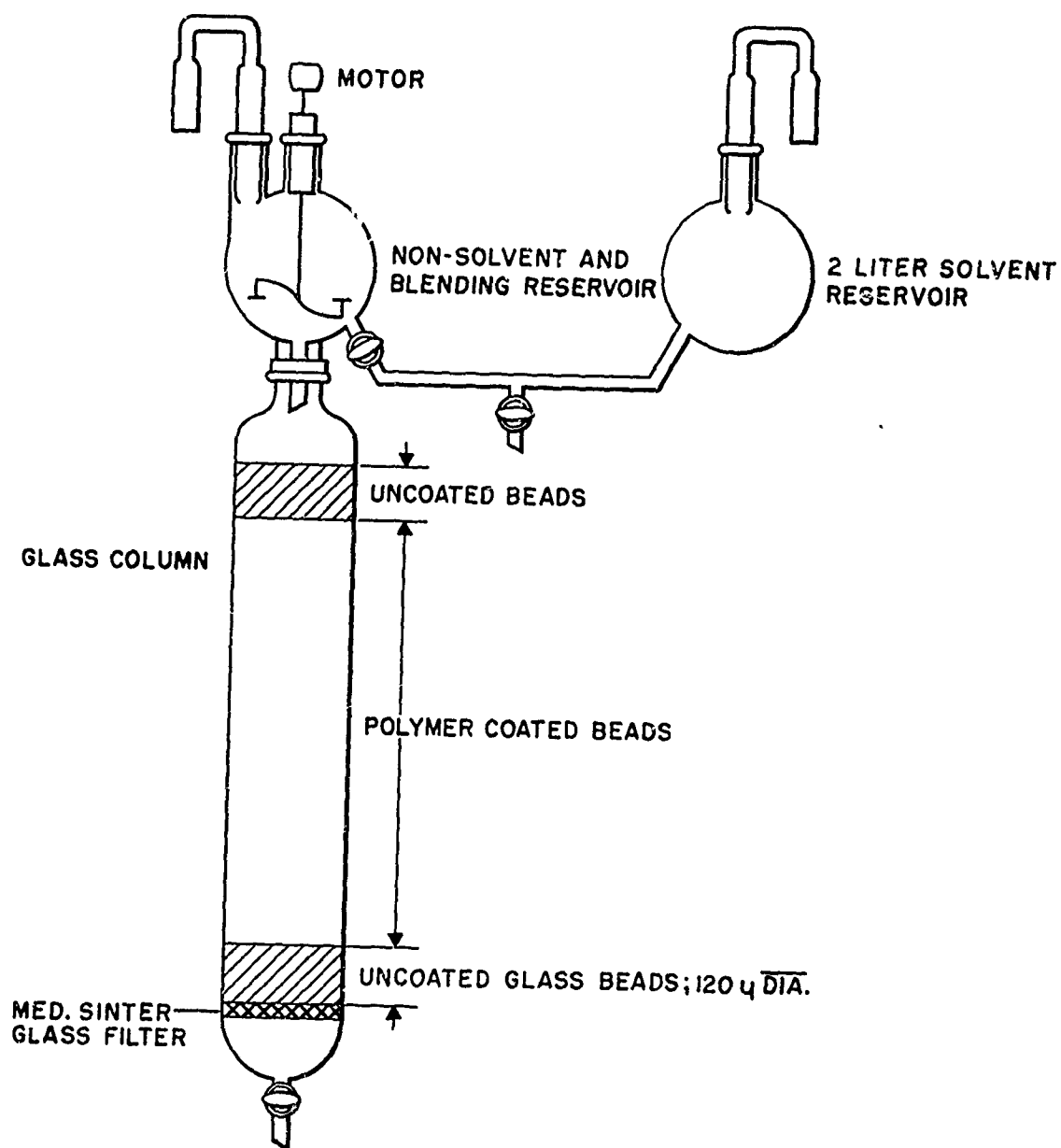


FIGURE 15. Fractionation Apparatus.

Gel Permeation Chromatography. - A Waters Gel Permeation Chromatograph, Type 100 was used under the following conditions:

Measurements in THF

Flow rate: 1 ml./min.

Temperature: 25°

Columns: 10^6 \AA , $8 \times 10^3 \text{ \AA}$, 10^3 \AA , $2.5 \times 10^2 \text{ \AA}$

Calibration: AK (see Figure 16)

Plate count: 557/ft. (DCB)

Total: 9,000 plates

Measurements in CHCl_3 :

Flow rate: 1 ml./min.

Temperature: 25°

Columns: 10^6 \AA , $8 \times 10^3 \text{ \AA}$, 10^3 \AA , $2.5 \times 10^2 \text{ \AA}$

Calibration: AQ (see Figure 17)

Plate count: 423/ft. (DCB)

Total: 6700 plates

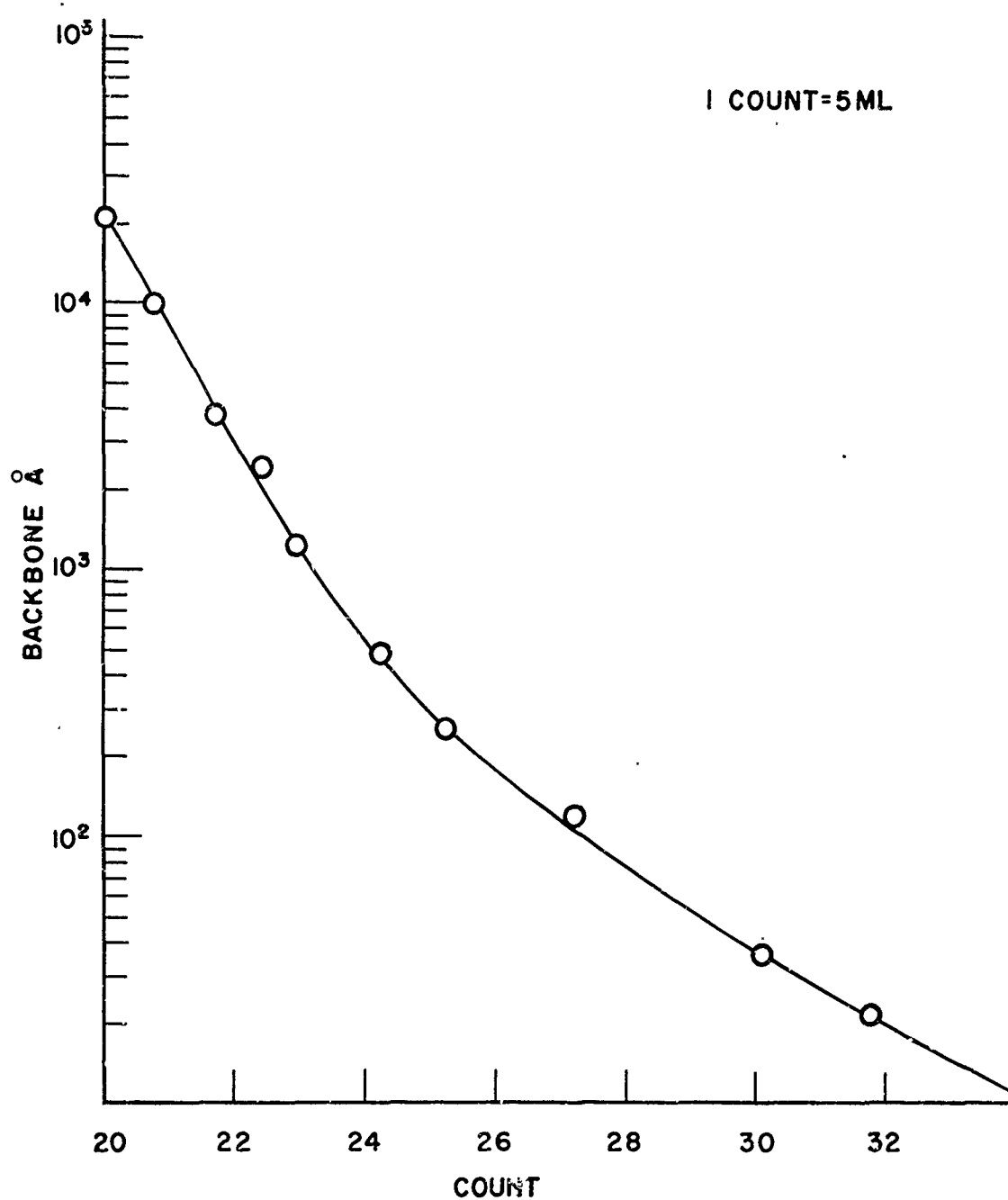


FIGURE 16. Calibration of Gel Permeation Chromatograph Calibration AK

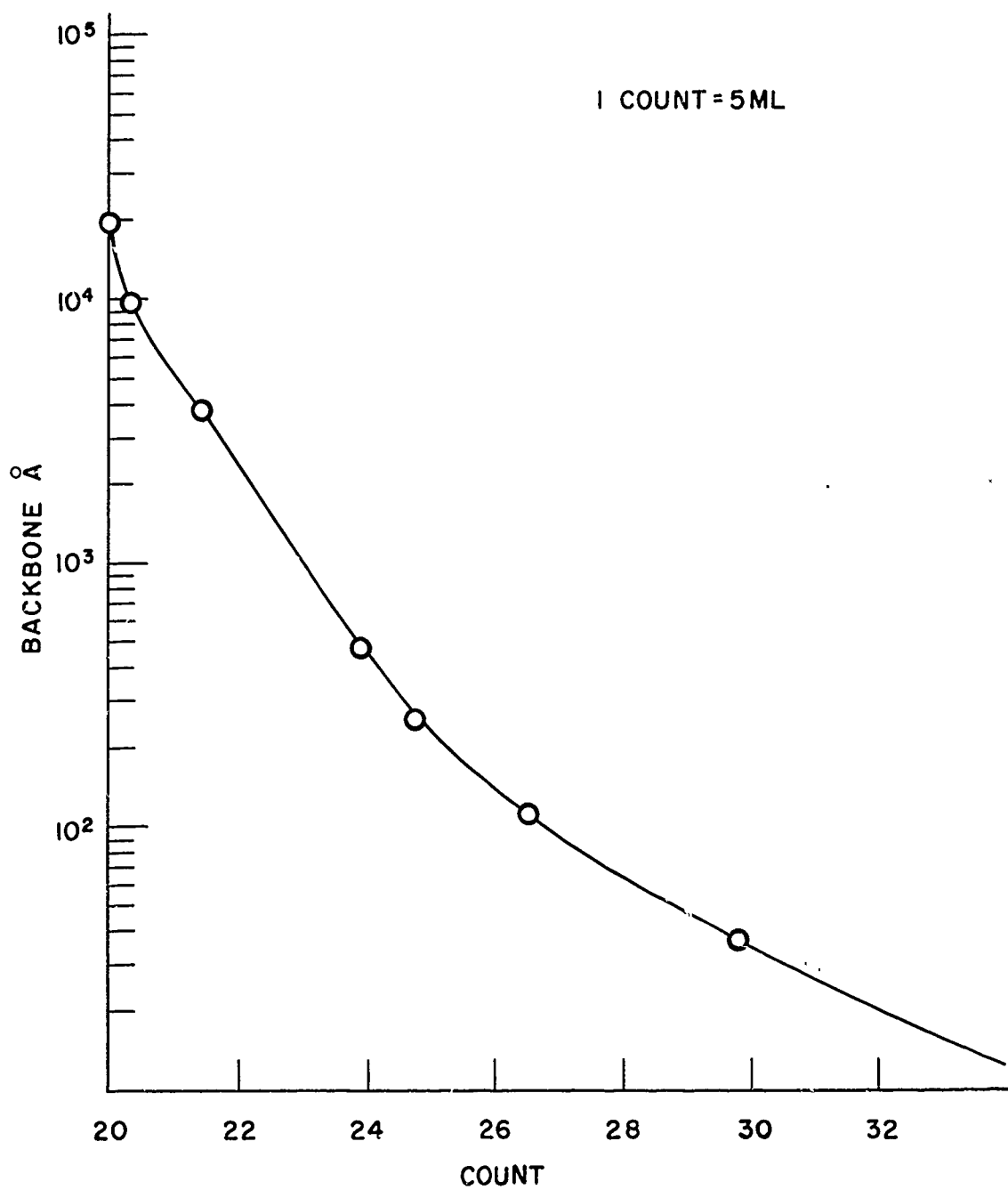


FIGURE 17. Calibration of Gel Permeation Chromatograph Calibration AQ

REFERENCES

1. P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, New York, 1953, p. 158.
2. British Patent 957,652, May 6, 1964.
3. Dutch Patent Appl. No. 6,504,864, Oct. 18, 1965.
4. R. M. Haines and W. A. Waters, *J. Chem. Soc.*, 4256(1955).
5. E. A. S. Cavell, *Makromol. Chemie.*, 54, 70(1962).
6. It is not understood why glutaric acid peroxide is satisfactory for the polymerization of butadiene and succinic acid peroxide is not. The latter is undoubtedly less hydrocarbon-soluble, but no problem was experienced in getting complete solution in the runs with succinic acid peroxide.
7. J. Blum and M. M. Delepine, *Compt. rend.* 248, 2883(1959).
8. Aerojet-General Corporation, Report BSD-TR-66-28, Vol. I, "Optimized Binder for High-Performance Solid Propellants."
9. G. Kraus and G. A. Moczygemba, *J. Polymer Sci.*, A2, 277(1964).
10. U. S. Patent 3,135,716, June 2, 1964.
11. D. P. Wyman, V. R. Allen and T. Altarcs, Jr., *J. Polymer Sci.*, A2, 4545(1964).
12. K. Hayashi and C. S. Marvel, *J. Polymer Sci.*, A2, 2571 (1964).
13. M. Morton, A. Rembaum and J. Hall, *J. Polymer Sci.*, A1, 461 (1963).
14. U. S. Patent 3,048,568, August 7, 1962.
15. British Patent 972,246, October 14, 1964.
16. British Patent 921,303, March 27, 1963.
17. Thiokol Chemical Corporation, Final Report TC 66-63, **Advancement of Solid Propellant Rocketry**, Army Supporting Research, Contract DA-01-021-ORD-1919, September 23, 1963.

TABLE I. (Appendix)
FREE RADICAL AMPOULE POLYMERIZATIONS
Ampoule Runs with Various Initiators

Run No.	BD ^a (g.)	Solvent (cc.)	ABIN ^b (g.)	ABCPA ^c (g.)	Calco 2246 (g.)	Temp. (°C.)	Time (hr.)	Conv. (%)	\bar{M}_n^{obs}	\bar{M}_n^{cor}	\bar{M}_{acid} (by IR)	$(\bar{M}_n/\bar{M}_{acid})$ Functionality
21	5	Dichlorobenzene 7		.26		97	1	2				
26-1	3.4	Acetone 6 Pyridine 9		.4	.005	88	46	6	1910	2155	620	3.5
28-1	5	Pyridine 15		.5	.005	112	22	26 6	1570	1590	610	2.6
26-Con	5	Pyridine 15	.05		.005	54 97	20 14	12	2730	2900	Control (No CO ₂ H)	
29-1	5	Pyridine 15		.5	.005	110	20	1% sol. .67 g. gel and residues				
31-1	5	Pyridine 15		.5	.025	109	22	2% sol. .76 g. gel and residues				

^aBD = butadiene; ^bABIN = azobisisobutyronitrile; ^cABCPA = 4,4'-azo-bis (4-cyanopentanoic acid);

TABLE II. (Appendix)
 FREE RADICAL AMPOULE POLYMERIZATIONS
 Ampoule Runs with Succinic Acid Peroxide (SAP) as Initiator

Run No.	Butadiene (g.)	Solvent (cc.)	SAP (g.)	Temp. (°C.)	Time (hr.)	Conversion (%)
A50a	5	15 Pyridine	—	101	2	0.4
50b	5	15 Pyridine	.05	100	2	1
50c	5	15 Pyridine	.1	100	2	1
50d	5	15 Pyridine	.2	100	2	2
50e	5	15 Pyridine	.3	100	2	1
50f	5	15 Pyridine	.5	100	2	2
A53a	5	15 Pyridine	0.2	100	2	2
53b	5	15 Pyridine	0.2	100	4	1
53c	5	15 Pyridine	0.2	100	6	2
53d	5	15 Pyridine	0.2	100	8	2
A53e	5	15 Pyridine	0.2	110	2	2
53f	5	15 Pyridine	0.2	110	4	1
53g	5	15 Pyridine	0.2	110	6	2
53h	5	15 Pyridine	0.2	110	8	2
B5a	5	15 Pyridine	0.4	110	4	2
5b	5	15 Pyridine	0.4	110	8	2
5c	5	15 Pyridine	0.6	110	4	2
5d	5	15 Pyridine	0.6	110	8	2
5e	5	15 Pyridine	0.8	110	5	2
5f	5	15 Pyridine	0.8	110	8	3 *
B16a	5	15:1 Dioxane-H ₂ O	0.8	95	2	2
16b	5	15:1 Dioxane-H ₂ O	0.8	95	5	3
16c	5	15:1 Dioxane-H ₂ O	0.8	96	6	3
16d	5	15:1 Dioxane-H ₂ O	0.8	96	8	4

* $\langle \eta \rangle$, 0.32

TABLE III. (Appendix)
FREE RADICAL POLYMERIZATIONS
GAP - Initiated Runs in Ampoules^a

Run No. (Notebook 18389)	Wt. of GAP (g.)	Temperature (°C.)	Time (hr.)	Conversion (%)	$\langle \eta \rangle$ (1% in C ₆ H ₆)	\bar{M}_v
24-A1	0.2	110	4	8	.16	7200
24-A2	0.6	110	4	20	.11	4500
24-A3	0.8	110	4	20	.08	3000
24-B1	0.6	70	4	14	.11	4500
24-B3	0.6	90	4	25	.12	5000
24-B3	0.6	100	4	24	.11	4500
26-B1	0.6	100	0.5	20		
26-B2	0.6	100	1	27		
26-B3	0.6	100	2	27		
26-A	0.6	100	4	24	.11	4500

^aAll runs contained 5 g. of butadiene and 15 cc. of purified tetrahydrofuran.

TABLE IV A. (Appendix) FREE RADICAL POLYMERIZATIONS
Laboratory Autoclave Runs with Glutaric Acid Peroxide (GAP) as Initiator

Run No.	GAP (g.)	Total Vol. of Soln. in Tetrahydrofuran (cc.)	Amt. of GAP Added per Aliquot (g.)	No. of Aliquots	Size of Aliquots (cc.)	Frequency of Addition (mins.)	Addition Time (hr.)	Temp. (°C.)
15	2.3	117	.12	19.5	6	15	4.5	95
24 26	3.0	75	.12	25	3	7.5	3	95
27 28	2.0	99	.12	16.5	6	7.5	2	95

TABLE IV B. (Appendix) FREE RADICAL POLYMERIZATIONS

Laboratory Autoclave Runs with Glutaric Acid Peroxide (GAP) as Initiator

Run No. (18974)	Conv. (%)	\bar{M}_{acid}	$\langle \eta \rangle$ (1% in C_6H_6)	Calco 2246 (% Found)	\bar{M}_n^{obs}	\bar{M}_n^{cor}	$F_{unc.}$ (\bar{M}_n/\bar{M}_{acid})	\bar{M}_v	\bar{M}_v/\bar{M}_{acid}
15A	21	1655	.22	1.0	5100	5950	3.6	10,900	6.6
15B		1665	.22	0.9	6100	7200	4.3	10,900	6.6
24	16	1435	.22	1.7	3000	3500	2.4	10,900	7.6
26	20	1310	.21	1.9	3500	4300	3.3	10,270	7.8
27	15	1315	.20	2.5	3000	3750	2.9	9,650	7.3
28	13	1265	—	2.9	2800	3600	2.8		—

(Sample 15 was divided into two portions for work-up: 15A was worked up by filtration of the cyclohexane-benzene solution, 15B by water-washing.)

TABLE IV C. (Appendix) FREE RADICAL POLYMERIZATIONS

Laboratory Autoclave Runs with Glutaric Acid Peroxide (GAP) as Initiator

Run no. (Notebook 18389)	Temp. (°C.)	Init. Addition (hr.)	Init. Conc. (g./aliquot)	Polymer Isolated* (% of Monomer)	Calco 2246 (%)	\bar{M}_{acid}	\bar{M}_n^{obs}	\bar{M}_n^{cor}	$\langle \eta \rangle$ (1% in C_6H_6)	\bar{M}_v	$F_{unc.}$ (\bar{M}_n/\bar{M}_{acid})	\bar{M}_v/\bar{M}_{acid}
38 ^b	100			12	0.6	1170	2430	2525	.20	9700	2.2	8.3
27	95	3:00	.521	32	2.0	1240	3160	3800	.20	9700	3.1	7.8
35	95	3:15	.948	28	3.3	535	1520	1725	.10	4000	3.2	7.5
35 re ^c							1570					
48	95	0:30	.971	3	1.3	1170	2280	2465	.10	4000	2.1	3.4
54	95	3:45	.485	7	1.4	1110	2030	2185	.13	5600	2.0	5.0
41	80	3:45	.243	5	12.0	1070	1370	2335	.13	5600	2.2	5.2
40	75	3:45	.485	7	10.9	800	1300	1985	.11	4500	2.5	5.6
53	75	3:30	.484	2	not detn.	880	1960	not detn.	.12	5000	not detn.	5.7
43	55	3:15	.480	1	-----	-----	-----	-----	-----	-----	-----	-----
51	55	3:50	.484	2	-----	-----	-----	-----	-----	-----	-----	-----

*Conversions were in many cases higher, but much polymer was lost in attempting to find suitable purification procedures.

^bData for the combined products of six identical ampoule runs (5 g. butadiene, 0.2 g. GAP, 15 cc. dioxane, 2 hours) are reported here for purposes of comparison. Note the breadth of the molecular weight distribution.

^cThis sample was re-worked to better remove suberic acid.

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Polymer Characterization
Polymer Fractionation
Gel Permeation Chromatography
Viscosity
Molecular Weight Measurement
Functionality
Chain Extension Studies
Synthesis Anionic
Synthesis Free Radical

ABSTRACT CARD

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